10/542,941 (FILE HOME' ENTERED AT 22:45:41 ON 19 MAR 2006)

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FILE 'REGISTRY' ENTERED AT 22:45:54 ON 19 MAR 2006
L1
                STRUCTURE UPLOADED
L2
             42 S L1
L3
            920 S L1 FULL
     FILE 'CAPLUS' ENTERED AT 22:46:30 ON 19 MAR 2006
L4
            250 S L3
L5
            231 S L4 AND PY<2003
L6
              6 S L5 AND PALLADIUM
L7
              3 S L5 AND PHOSPHINE
=> d 15 1-231 bib abs
L5
     ANSWER 1 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
AN
     2002:117127 CAPLUS
DN
     137:46771
TI
     Bromine-magnesium exchange in gem-dibromocyclopropanes using Grignard
AU
     Baird, Mark S.; Nizovtsev, Alexey V.; Bolesov, Ivan G.
CS
     Department of Chemistry, University of Wales, Bangor, Gwynedd, LL57 2UW,
SO
     Tetrahedron (2002), 58(8), 1581-1593
     CODEN: TETRAB; ISSN: 0040-4020
PB
     Elsevier Science Ltd.
DT
     Journal
LA
     English
os
     CASREACT 137:46771
AB
     Reaction of gem-dibromocyclopropanes with ethylmagnesium bromide at
     ambient temperature leads to very high yields of allenes, e.g. 96%
     3-phenylbuta-1,2-diene. When cyclopropylidene-allene ring opening is
     suppressed, alternative carbenic products are observed, although other
     reactions compete. When the reactions were carried out at -60°, a
     1-bromo-1-(bromomagnesio)cyclopropane is formed which may be trapped by a
     number of electrophiles.
RE.CNT 87
              THERE ARE 87 CITED REFERENCES AVAILABLE FOR THIS RECORD
              ALL CITATIONS AVAILABLE IN THE RE FORMAT
L5
     ANSWER 2 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
AN
     2001:530533 CAPLUS
DN
     135:268418
TΙ
     On the PNN modeling of estrogen receptor binding data for carboxylic acid
     esters and organochlorine compounds
ΑU
     Kaiser, Klaus L. E.; Niculescu, Stefan P.
CS
     National Water Research Institute, Burlington, ON, L7R 4A6, Can.
SO
     Water Quality Research Journal of Canada (2001), 36(3), 619-630
     CODEN: WORCFA; ISSN: 1201-3080
PΒ
     Canadian Association on Water Ouality
DT
     Journal
LA
AB
     The authors describe the relationship between the estrogen receptor
     binding and the mol. structure of chems. using the probabilistic neural
     network methodol. with structural fragment descriptors as input variables
     and a data set of 1118 compds. Exploratory models identified two subsets
     of chems. for which the predictions were well correlated with the measured
     values, namely chlorine-containing compds. and carboxylic esters, and for
     which individual models were developed. Both compound classes are in the
     classification system for chems. on the Canadian Domestic Substances List
     (DSL) and the data cover five orders of magnitude in activity in each of
     these classes. The results show excellent performance of both models and
     are highly encouraging in the search for other models for this and other
     receptor binding data as well as other classes of DSL substances.
     also confirm the flexibility, usefulness and applicability of the
    probabilistic neural networks as modeling methodol. to a wide variety of
    modeling challenges in the environmental and health fields.
RE.CNT 11
              THERE ARE 11 CITED REFERENCES AVAILABLE FOR THIS RECORD
```

ALL CITATIONS AVAILABLE IN THE RE FORMAT

```
ANSWER 3 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
L5
AN
     2001:222245 CAPLUS
DN
     135:45862
ΤI
     A novel cis-trans photoisomerization of vinylidenecyclopropanes via an
     electron-transfer chain process
     Mizuno, K.; Nire, K.; Sugita, H.; Maeda, H.
ΑU
     Graduate School of Engineering, Department of Applied Chemistry, Osaka
CS
     Prefecture University, Sakai, Osaka, 599-8531, Japan
     Tetrahedron Letters (2001), 42(14), 2689-2692
SO
     CODEN: TELEAY; ISSN: 0040-4039
PΒ
     Elsevier Science Ltd.
DT
     Journal
     English
LA
     The cis-trans photoisomerization of 1,1-bis(4-methoxyphenyl)vinylidene-2,3-
AB
     dimethylcyclopropanes in aerated MeCN was sensitized by
     9,10-dicyanoanthracene and chloranil in the presence of an additive via an
     electron-transfer chain process, in which the cation radicals generated
     from the vinylidenecyclopropanes were involved as chain carriers.
RE.CNT 29
              THERE ARE 29 CITED REFERENCES AVAILABLE FOR THIS RECORD
              ALL CITATIONS AVAILABLE IN THE RE FORMAT
L5
     ANSWER 4 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
AN
     2000:293423 CAPLUS
DN
     133:104818
     Regio- and endo-Selective [2 + 2] Photocycloadditions of Homobenzoquinones
ΤI
     with Ethyl Vinyl Ether
     Kokubo, Ken; Nakajima, Yu-ichi; Iijima, Katsuyuki; Yamaguchi, Hiroshi;
ΑU
     Kawamoto, Tatsuya; Oshima, Takumi
CS
     Department of Applied Chemistry Faculty of Engineering, Osaka University,
     Toyonaka Osaka, 560-0043, Japan
SO
     Journal of Organic Chemistry (2000), 65(11), 3371-3378
     CODEN: JOCEAH; ISSN: 0022-3263
PB
     American Chemical Society
DT
     Journal
LA
     English
os
     CASREACT 133:104818
     Irradiation of various meta- and para-substituted homobenzoquinones with Et
AΒ
     vinyl ether gave the [2 + 2] photoadducts, tricyclic diones, regio- and
     endo-selectively and in good yields. The tricyclic skeleton has an
     anti-configuration built by the addition of Et vinyl ether from the less
     hindered side of the homoquinones. All of the substituents (Me, Cl, Br,
     MeO) at the reacting C:C double bond afforded head-to-head (HH) addition
     predominantly. In the case of Me, Cl, and Br, the ethoxy group was
     oriented in the endo-position, while the MeO substituent led to a 1/5
     mixture with the exo-isomer. It was also found that the Br-substituted [2 +
     2] adducts undergo a facile skeletal rearrangement, being converted into
     dihydro-o-benzoquinone monomethide derivs. for para-substitution and
     dihydrobenzofuran derivs. for meta-substitution, probably under the
     influence of the in situ generated HBr. Intramol. [2 + 2] photocycloaddn.
     of an alkenylhomobenzoquinone afforded a tetracyclic dione.
RE.CNT 73
              THERE ARE 73 CITED REFERENCES AVAILABLE FOR THIS RECORD
              ALL CITATIONS AVAILABLE IN THE RE FORMAT
L5
     ANSWER 5 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
AN
     2000:119805 CAPLUS
DN
     132:222125
TI
     Kinetic study of thermolysis of diarylhomonaphthoguinones. Endo/exo
     substituent and solvent effects
ΑU
     Oshima, Takumi; Tamada, Kazushi; Tamura, Hatsue; Nagai, Toshikazu
CS
     Department of Applied Chemistry, Faculty of Engineering, Osaka University,
     Osaka, 560, Japan
SO
     Perkin 2 (2000), (1), 135-141
     CODEN: PRKTFO
PB
     Royal Society of Chemistry
```

DT

LA GI Journal English

Ι

AB The kinetics of thermal cyclopropane ring-opening of a series of m- and p-substituted endo/exo diphenylbromohomonaphthoquinones and the unsubstituted diphenylchlorohomonaphthoquinone have been investigated and compared with biphenyl-2,2'-diylhalogenohomonaphthoquinones . first-order rate consts. k/s-1 at 100° in toluene increased with the electron-donating ability of the substituents. The kinetics substituent effects were much more pronounced for the exo family than for the endo one and revealed the crucial role of the resonance contribution of diaryl groups; $log (k/ko) exo = -1.99\sigma + + 0.086$ and log (k/ko) endo= -0.784 σ + + 0.002, resp. The kinetic solvent effects on the thermolysis of representative compound I were so minute that the rates tended to slightly increase with the solvent polarity but decrease with the solvent basicity. These kinetic results were interpreted in terms of a concerted disrotatory ring opening of the incorporated cyclopropane ring.

RE.CNT 56 THERE ARE 56 CITED REFERENCES AVAILABLE FOR THIS RECORD ALL CITATIONS AVAILABLE IN THE RE FORMAT

L5 ANSWER 6 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN

AN 1999:798100 CAPLUS

DN 132:151874

TI 1,3-Dipolar cycloaddition of diazoalkanes to racemic and optically active α -(diethoxyphosphoryl)vinyl p-tolyl sulfoxides: a new synthesis of 3-phosphorylpyrazoles and asymmetric synthesis of cyclopropanes

AU Midura, Wanda H.; Krysiak, Jerzy A.; Mikolajczyk, Marian

CS Centre of Molecular and Macromolecular Studies, Department of Organic Sulfur Compounds, Polish Academy of Sciences, Lodz, 90-363, Pol.

SO Tetrahedron (1999), 55(51), 14791-14802 CODEN: TETRAB; ISSN: 0040-4020

PB Elsevier Science Ltd.

DT Journal

LA English

OS CASREACT 132:151874

GΙ

Cycloaddn. of diazomethane and Et diazoacetate to α - (diethoxyphosphoryl)vinyl p-tolyl sulfoxide la and its β -substituted analogs (Me, Ph) gave 3-phosphorylpyrazoles in high yield. The reaction of chiral (S)-(+)-la with diphenyldiazomethane proceeds fully diastereoselectively to give the corresponding cyclopropane (+)-I (86% yield) with the (SC,SS) configuration determined by x-ray diffraction anal. Diazopropane reacts with (S)-(+)-la to give only one diastereoisomer of the pyrazoline cycloadduct (+)-II (90% yield) which undergoes decomposition to the cyclopropane (+)-6b with preservation of configurational integrity.

RE.CNT 19 THERE ARE 19 CITED REFERENCES AVAILABLE FOR THIS RECORD

ALL CITATIONS AVAILABLE IN THE RE FORMAT L5ANSWER 7 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN 1999:369130 CAPLUS ANDN 131:26016 2-Bromo-2, 3-diphenylmethano-2, 3-dihydronaphthoquinone ΤI Oshima, Takumi; Fukushima, Kazuaki; Kawamoto, Tatsuya ΑU Department of Applied Chemistry, Faculty of Engineering, Osaka University, CS Osaka, 560-0043, Japan Acta Crystallographica, Section C: Crystal Structure Communications (SO 1999), C55(4), 608-610 CODEN: ACSCEE; ISSN: 0108-2701 PB Munksquard International Publishers Ltd. DTJournal LA English AB In the title compound, a diphenylhomonaphthoquinone, C23H15BrO2, the quinone frame adopts a slightly boat-shaped conformation, with folding angles of 11(3) and 14(3)°. The severe steric congestion between the endo-Ph group and the quinone moiety results in considerable freezing of the aromatic ring. Crystallog. data are given. THERE ARE 9 CITED REFERENCES AVAILABLE FOR THIS RECORD RE.CNT 9 ALL CITATIONS AVAILABLE IN THE RE FORMAT ANSWER 8 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN L5 1999:148536 CAPLUS ANĎΝ 130:281805 TIThe gem-dihaloarylcyclopropanes in reactions with sodium nitrate in trifluoroacetic and sulfuric acids Saginova, L. G.; Alhamdan, Mohammad; Petrosyan, V. S. AU CS Kafedra Org. Khim., MGU, Russia Vestnik Moskovskogo Universiteta, Seriya 2: Khimiya (1998), SO 39(5), 339-343 CODEN: VMUKA5; ISSN: 0579-9384 PB Izdatel'stvo Moskovskogo Universiteta DT Journal LA Russian Reaction of 1,1-dichloro- and 1,1-dibromo-2-phenylcyclopropane (I) with AB NaNO3 in CF3CO2H resulted in nitration of the aromatic ring in the ortho and para positions. In the case of I, CF3CO2CHPhCH2CBr2NO was also formed. When the reactions were carried out in concentrated H2SO4, the main products were 5-halo-3-(4-nitrophenyl)isoxazoles. Reaction of 1,1-dibromo-2,2diphenylcyclopropane with NaNO3 in concentrated H2SO4 resulted in nitration of one or both aromatic rings in the para position. L5 ANSWER 9 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN 1998:489032 CAPLUS ANDN 129:230468 Synthesis and biological evaluation of cyclopropyl analogs of the TI antiestrogen MER 25 AU Overacre, Lynette B.; Magarian, Robert A. Med. Chem./Pharmaceutics Dep., Coll. Pharmacy, Univ. Oklahoma Health Sci. CS Cent., Oklahoma City, OK, 73190, USA SO Bioorganic Chemistry (1998), 26(1), 15-31 CODEN: BOCMBM; ISSN: 0045-2068 PB Academic Press

DT

LA

GI

Journal

English

1

In an effort to prepare effective nonsteroidal antiestrogens without AB intrinsic estrogenicity and with greater antagonism than the triarylethylenes (tamoxifen), four (E)- and (Z)-1,1-dichloro-2-phenyl-2-[4-(2-diethylaminoethoxy)phenyl]-3-(4-methoxyphenyl)cyclopropane analogs (E)and (Z)-I (R1 = OCH2CH2NEt2, R2 = MeO, R3 = H) <math>(II) and (E)- and (Z)-I (R1)= OCH2CH2NEt2, R2 = MeO, OC7F7) (III) of the antiestrogen MER 25 were prepared The (E) - and (Z) -gem-dichlorotriarylcyclopropanes were tested for their ability to inhibit the growth of estrogen receptor (ER)-pos. MCF-7E3 and ER-neq. MDA-MB-231 human breast cancer cells in culture. All compds., except (E)-III, exhibited a statistically significant (P < 0.01) reduction in estradiol-stimulated growth (antiestrogenic activity) at 1.0 µM concentration in the MCF-7E3 cells. Inhibition of estradiol-stimulated growth at concns. lower than 1.0 μM was demonstrated by (E)-II, MER 25, and ICI (E)-II produced weak inhibition at 0.1 nM (19%) and nearly complete inhibition (79-112%) over a concentration range of 1.0 to 100 nM. 25 produced inhibition of estradiol-stimulated growth at 1.0 (39%), 10 (102%), and 100 nM (100%) concns. ICI 182,780 completely inhibited estrogen-stimulated growth from 0.1 nM to 1.0 µM concns. Two compds. exhibited estrogenic activity: (E)-III (from 1.0 nM to 1.0 μ M concns.) and MER 25, which had antiestrogenic action at the lower concentration ranges, but exhibited estrogenic properties at 100 nM to 1.0 µM concns. None of the test compds. or stds. were active in the MDA-MB-231 cell line at the concns. studied (0.01 nM to 1.0 μ M). In addition, none of the compds. inhibited cell growth below control in the MCF-7E3 cell line. The results from both cell lines suggest that the test compds. are devoid of any antitumor properties, which is thought to be mediated through a nonreceptor mechanism. Analog (E)-II has the potential to be useful in the treatment of hormone-responsive breast cancer. (c) 1998 Academic Press.

RE.CNT 31 THERE ARE 31 CITED REFERENCES AVAILABLE FOR THIS RECORD ALL CITATIONS AVAILABLE IN THE RE FORMAT

L5 ANSWER 10 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN

AN 1998:480666 CAPLUS

DN 129:203008

- TI Reactivity of the acids of trivalent phosphorus and their derivatives.

 Part IX. The >P-O- and >P-S- nucleophiles in the reactions of halophilic substitution
- AU Dembkowski, Leszek; Witt, Dariusz; Rachon, Janusz
- CS Dep. of Organic Chemistry, Chemical Faculty, Technical University of Gdansk, Gdansk, 80-952, Pol.
- SO Phosphorus, Sulfur and Silicon and the Related Elements (1997), 127, 143-157
 - CODEN: PSSLEC; ISSN: 1042-6507 Gordon & Breach Science Publishers
- DT Journal

PB

- LA English
- AB The reaction of the >P-Y- (Y = 0, S) nucleophiles with the compds. possessing a C-Br bond and electron-withdrawing groups (Me 1-bromo-2,2-diphenylcyclopropanecarboxylate, p-nitrobenzyl bromide; bromodiphenylmethane, 9-bromofluorene, bromotriphenylmethane) is described. The isolation of the products derived from dialkyl bromophosphates, the results of the 31P NMR studies, as well as the isolation of bromothiophosphate from the reaction mixture of >P-S-nucleophile and Me α -bromocarboxylate, are further evidence for

halophilic substitution as the principal process in the X-philic substitution/SET tandem mechanism operating in the reaction of these P nucleophiles with the bromo derivs. possessing electron-withdrawing groups.

RE.CNT 34 THERE ARE 34 CITED REFERENCES AVAILABLE FOR THIS RECORD ALL CITATIONS AVAILABLE IN THE RE FORMAT

- L5 ANSWER 11 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
- AN 1998:355637 CAPLUS
- DN 129:109218
- TI Synthesis of tri-(-)-menthyltin hydride and stereoselective reduction of some halocyclopropane derivatives
- AU Radivoy, Gabriel E.; Koll, Liliana C.; Podestra, Julio C.
- CS Inst. Investigaciones Quim. Org., Dep. Quim. Ingenieria Quim., Univ. Nacional Sur, Bahia Blanca, 8000, Argent.
- SO Anales de la Asociacion Quimica Argentina (1997), 85(5-6), 295-300
 - CODEN: AAQAAE; ISSN: 0365-0375
- PB Associacion Quimica Argentina
- DT Journal
- LA English
- OS CASREACT 129:109218
- AB The synthesis and phys. properties of tri-(-)-menthyltin hydride and chloride are reported. Free radical reduction of achiral 1,1-dichloro-2,2-diphenylcyclopropane and Me (R)-(+)-1-bromo-2,2-diphenylcyclopropanecarboxylate with tri-(-)-menthyltin hydride led to the corresponding optically active dehydrohalogenation products, thus showing that these reactions are stereoselective. Full 1H, 13C, and 119Sn NMR data are given.
- RE.CNT 20 THERE ARE 20 CITED REFERENCES AVAILABLE FOR THIS RECORD ALL CITATIONS AVAILABLE IN THE RE FORMAT
- L5 ANSWER 12 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
- AN 1998:342143 CAPLUS
- DN 129:95554
- TI Diastereoselective asymmetric cyclopropanation of $(S)-(+)-\alpha-(diethoxyphosphoryl)$ vinyl p-tolyl sulfoxide
- AU Midura, Wanda H.; Krysiak, Jerzy A.; Wieczorek, Michal W.; Majzner, Wieslaw R.; Mikolajczyk, Marian
- CS Centre of Molecular and Macromolecular Studies, Department of Organic Sulfur Compounds, Polish Academy of Sciences, Lodz, 90-363, Pol.
- SO Chemical Communications (Cambridge) (1998), (10), 1109-1110 CODEN: CHCOFS; ISSN: 1359-7345
- PB Royal Society of Chemistry
- DT Journal
- LA English

GΙ

OS CASREACT 129:95554

AB The title sulfoxide 1 reacts with fully deuterated dimethylsulfoxonium methylide, diphenylsulfonium isopropylide and diphenyldiazomethane to form the corresponding cyclopropanes, e.g. I, as single diastereoisomers; the chirality of the cyclopropane (+)-I obtained from 1 and diphenyldiazomethane is (SS,SC) as determined by x-ray diffraction anal.; based on exptl. data, the steric course of the asym. cyclopropanation is

proposed.

RE.CNT 11 THERE ARE 11 CITED REFERENCES AVAILABLE FOR THIS RECORD ALL CITATIONS AVAILABLE IN THE RE FORMAT

- L5 ANSWER 13 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
- AN 1997:594517 CAPLUS
- DN 127:234171
- TI Preparation of diphenylcyclopropanes as antiestrogens
- IN Magarian, Robert A.; Pento, Joseph T.; Overacre, Lynette
- PA Research Corporation Technologies, USA
- SO U.S., 36 pp., Cont.-in-part of U.S. Ser. No. 376,961.
 - CODEN: USXXAM
- DT Patent
- LA English
- FAN.CNT 7

FAN.	CNT /				
	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PΙ	US 5658951	A	19970819	US 1995-487717	19950607 <
	US 4879315	A	19891107	US 1987-98945	19870921 <
	US 5098903	Α	19920324	US 1989-432564	19891106 <
	US 5397802	A	19950314	US 1993-20922	19930222 <
	US 5663207	Α	19970902	US 1995-376961	19950120 <
PRAI	US 1980-128040	B2	19800307		
	US 1980-166255	B2	19800707		
	US 1982-363429	B2	19820330		
	US 1987-98945	A2	19870921		
	US 1989-432564	A2	19891106		
	US 1991-812246	B2	19911219		
	US 1993-20922	A1	19930222		
	US 1995-376961	A2	19950120		
os	MARPAT 127:234171				
GI					

$$\begin{array}{c|cccc}
R^1 & R^2 \\
R & & R^3 \\
R & & R^4 & I
\end{array}$$

- AB Title compds. [I; R = H or halo; R1,R4 = H or alkyl; R2,R3 = (un)substituted Ph] were prepared Thus, I [R = Cl R1 = R4 = H R2 = Ph, R3 = C6H4(OCH2CH2R5)-4](II; R5 = OSO2Me)(preparation given) was condensed with piperidine to give II (R5 = piperidino). Data for biol activity of I were given.
- L5 ANSWER 14 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
- AN 1997:594516 CAPLUS
- DN 127:234170
- TI Preparation of diphenylcyclopropanes as antiestrogens
- IN Magarian, Robert A.; Pento, Joseph T.; Overacre, Lynette
- PA Research Corporation Technologies, USA
- SO U.S., 36 pp., cont.-in-part of U. S. Ser. No. 376,961. CODEN: USXXAM
- DT Patent
- LA English
- FAN. CNT 7

FAN. CNT /				
PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI US 5658927	A	19970819	US 1995-480212	19950607 <
US 4879315	Α	19891107	US 1987-98945	19870921 <
US 5098903	Α	19920324	US 1989-432564	19891106 <
US 5397802	Α	19950314	US 1993-20922	19930222 <
US 5663207	Α	19970902	US 1995-376961	19950120 <
PRAI US 1980-128040	B2	19800307		
US 1980-166255	B2	19800707		

τ	JS	1982-363429	B2	19820330
τ	JS	1987-98945	A2	19870921
τ	JS	1989-432564	A2	19891106
τ	JS	1991-812246	B2	19911219
τ	JS	1993-20922	A1	19930222
τ	JS	1995-376961	A2	19950120
N	1AF	RPAT 127:234170		

GI

os

AB Title compds. [I; R = H or halo; R1,R4 = H or alkyl; R2,R3 = (un)substituted Ph] were prepared Thus, I [R = Cl R1 = R4 = H R2 = Ph, R3 = C6H4 (OCH2CH2R5)-4] (II; R5 = OSO2Me) (preparation given) was condensed with piperidine to give II (R5 = piperidino). Data for biol activity of I were given.

L5 ANSWER 15 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN

AN 1997:594515 CAPLUS

DN 127:234122

TI Diphenylcyclopropanes as antiestrogens and antitumor agents

IN Magarian, Robert A.; Pento, Joseph T.; Overacre, Lynette

PA Research Corporation Technologies, USA

SO U.S., 35 pp., Cont.-in-part of U. S. Ser. No. 376,961.

CODEN: USXXAM

DT Patent

LA English

FAN.CNT 7

L. LTA.	CNI /				
	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	US 5658914	A	19970819	US 1995-480215	19950607 <
	US 4879315	Α	19891107	US 1987-98945	19870921 <
	US 5098903	Α	19920324	US 1989-432564	19891106 <
	US 5397802	Α	19950314	US 1993-20922	19930222 <
	US 5663207	Α	19970902	US 1995-376961	19950120 <
PRAI	US 1980-128040	B2	19800307		
	US 1980-166255	B2	19800707		
	US 1982-363429	B2	19820330		
	US 1987-98945	A2	19870921		
	US 1989-432564	A2	19891106		
	US 1991-812246	B2	19911219		
	US 1993-20922	A1	19930222		
	US 1995-376961	A2	19950120		
os	MARPAT 127:234122				
GI					

$$R^2$$
 R^4
 R^4

AΒ

Diphenylcyclopropanes I [X = H, Cl; R1, R4 = H, alkyl; R2, R3 = H, piperazinoalkoxy] were prepared for use as antiestrogens and anti-tumor

Ι

agents. Thus, cis-stilbene was treated with PhMgCBrCl2 under reflux to give 86% cis-1,1-dichloro-2,3-diphenylcyclopropane which had an IC50 for inhibition of the uterotropic activity of estradiol of 36 μg .

- L5 ANSWER 16 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
- AN 1997:411514 CAPLUS
- DN 127:46457
- TI Quantitative structure-activity relationships of DDT-type compounds in a sodium tail-current in crayfish giant axons
- AU Nishimura, Keiichiro; Okimoto, Hiroshi
- CS Research Institute Advanced Science and Technology, Osaka Prefecture Univ., Sakai, Osaka, 593, Japan
- SO Pesticide Science (1997), 50(2), 104-110 CODEN: PSSCBG; ISSN: 0031-613X
- PB Wiley
- DT Journal
- LA English
- Effects of DDT-type compds. including 1,1-bis(para-substituted AB phenyl)-2,2-dichlorocyclopropanes (DCC-series compds.) on sodium currents in crayfish giant axons were measured under voltage-clamp conditions. Variations in the activity to prolong the tail-current that was observed upon step repolarization of the membrane were quant. analyzed by use of physicochem. parameters of aromatic substituents and regression anal. Introduction of lengthy and narrow substituents was favorable to the activity. Variations in the activity were parabolically related to the hydrophobicity, optimum value being around that of H. DDT- and prolan-series compds. were 203 times more active than DCC-series compds. when other structural factors were the same. Insecticidal activity of the compds. was linearly correlated with the tail-current activity when the hydrophobic factor for sep. considered. The insecticidal activity of DDT-series compds. was 2.5 times higher than that of others when the other factors were the same.
- L5 ANSWER 17 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
- AN 1997:338226 CAPLUS
- DN 127:50883
- TI A molecular modeling study on the interaction between $\beta\mbox{-cyclodextrin}$ and synthetic pyrethroids
- AU Manunza, Bruno; Deiana, Salvatore; Pintore, Marco; Delogu, G.; Gessa, Carlo
- CS DISAABA, Universita di Sassari, Sassari, 07100, Italy
- SO Carbohydrate Research (1997), 300(1), 89-93 CODEN: CRBRAT; ISSN: 0008-6215
- PB Elsevier
- DT Journal
- LA English
- AB The interaction between four cycloprothrin derivs. and β -cyclodextrin was investigated by means of mol. dynamics. Several in vacuo trajectories were calculated for each system imposing a 1:1 stoichiometry. Moreover, for one particular guest-host couple, the 1:2 guest-host ratio was investigated. We also took into account the influence of the solvent and of the temperature. The results account for the formation of adducts which are stable at room temperature. The formation of the adduct involves the Ph groups of the guest mols. which mainly interact with the hydrophobic cavity of the host by van der Waals forces.
- RE.CNT 15 THERE ARE 15 CITED REFERENCES AVAILABLE FOR THIS RECORD ALL CITATIONS AVAILABLE IN THE RE FORMAT
- L5 ANSWER 18 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
- AN 1997:314569 CAPLUS
- DN 127:5177
- TI New complexes of platinum(0) with cyclopropenes
- AU Hughes, David L.; Leigh, G. Jeffery; Mcmahon, C. Niamh
- CS Nitrogen Fixation Laboratory, John Innes Centre, Norwich Research Park, Norwich, NR4 7UH, UK
- Journal of the Chemical Society, Dalton Transactions: Inorganic Chemistry
 (1997), (8), 1301-1307
 CODEN: JCDTBI; ISSN: 0300-9246
- PB Royal Society of Chemistry

- DT Journal
- LA English
- AB New cyclopropene complexes of Pt were synthesized with a variety of bulky substituents on all positions of the cyclopropene ring. Two of these novel complexes, [Pt(3,3-Ph2C3H2)(PPh3)2] and [Pt(1,2-Ph2C3H2)(PPh3)2], were structurally characterized by x-ray anal. Both contain a cyclopropene ring which has remained intact upon complexation. The bond lengths within the complexes are remarkably independent of the substituents. The structural characteristics and the 31P NMR spectra of these complexes are discussed. Pt cyclopropene complexes were prepared by substitution reaction of (ethene)bis(triphenylphosphine)platinum directly with the substituted cyclopropenes.
- RE.CNT 35 THERE ARE 35 CITED REFERENCES AVAILABLE FOR THIS RECORD ALL CITATIONS AVAILABLE IN THE RE FORMAT
- L5 ANSWER 19 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
- AN 1996:596335 CAPLUS
- DN 125:300480
- TI Reaction of gem-dihalocyclopropanes with nucleophilic reagents: formation of acetylene derivatives and mechanism of reaction
- AU Kostikov, R. R.; Varakin, G. S.; Molchanov, A. P.; Ogloblin, K. A.
- CS St. Peterburg. Gos. Univ., St. Petersburg, 198904, Russia
- SO Zhurnal Organicheskoi Khimii (1996), 32(1), 39-43 CODEN: ZORKAE; ISSN: 0514-7492
- PB Nauka
- DT Journal
- LA Russian
- AB Heating gem-dibromocyclopropanes with KOH in alcs. gave cyclopropanone acetals and propargylic ethers. The mechanism of product formation was discussed.
- L5 ANSWER 20 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
- AN 1996:584239 CAPLUS
- DN 125:300511
- TI Thermal reactions of gem-dihalocyclopropanes: alkylation of aromatic compounds and reaction with nucleophilic reagents
- AU Kostikov, R. R.; Varakin, G. S.; Molchanov, A. P.; Ogloblin, K. A.
- CS St. Peterburg. Gos. Univ., St. Petersburg, 198904, Russia
- SO Zhurnal Organicheskoi Khimii (1996), 32(3), 367-371 CODEN: ZORKAE; ISSN: 0514-7492
- PB Nauka
- DT Journal
- LA Russian
- AB Heating 1,1-dihalo-2-phenylcyclopropanes in aromatic solvents at 140-165° resulted in electrophilic aromatic alkylation. Heating 1,1-dibromo-2,3-diphenylcyclopropane with nucleophiles RH (R = BuO, MeOCH2CH2O, morpholino, PhNH) at 120° gave PhCH:CBrCHRPh.
- L5 ANSWER 21 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
- AN 1996:501487 CAPLUS
- DN 125:221311
- TI A Novel Type of Cyanomethylation Reaction of Diarylethenes with Acetonitrile Photosensitized by Benzophenone in the Presence of tert-Butylamine
- AU Yamashita, Toshiaki; Yasuda, Masahide; Watanabe, Motonori; Kojima, Ryuji; Tanabe, Kimiko; Shima, Kensuke
- CS Department of Chemical Science and Engineering, Miyakonojo National College of Technology, Miyakonojo, 885, Japan
- SO Journal of Organic Chemistry (1996), 61(18), 6438-6441 CODEN: JOCEAH; ISSN: 0022-3263
- PB American Chemical Society
- DT Journal
- LA English
- OS CASREACT 125:221311
- AB The cyanomethylation of 1,1-diphenylethene (I) efficiently occurred upon photosensitization by benzophenone in the presence of tert-butylamine in acetonitrile to give 4,4-diphenylbutanenitrile in 77% yield. It was confirmed that tert-butylamine is essential for the benzophenone-photosensitized cyanomethylation, since no or negligible cyanomethylation

was effected in the absence of the amine or by using such other amines as i-PrNH2, Et2NH, and Et3N. The benzophenone photosensitization in the presence of tert-butylamine was successfully applied to the cyanomethylation of some other diarylethenes and also to the alkylations of I with propionitrile, dichloromethane, chloroform, and acetone used as solvent.

- L5 ANSWER 22 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
- AN 1996:457357 CAPLUS
- DN 125:221226
- TI Dimethyldioxirane oxidations of some cyclopropanes
- AU Dehmlow, Eckehard Volker; Heiligenstaedt, Noemi
- CS Fak. Chem., Univ. Bielefeld, Bielefeld, D-33501, Germany
- SO Tetrahedron Letters (1996), 37(30), 5363-5364
- CODEN: TELEAY; ISSN: 0040-4039
- PB Elsevier
- DT Journal
- LA English
- AB Phenylcyclopropanes and halo-phenyl-substituted cyclopropanes do not react with dimethyldioxirane. Bicyclo[4.1.0]heptane, however, is oxidized by this reagent to the 2-ketone. Bicyclo[6.1.0]nonane gives all three possible ketones. Even exo-9-bromobicyclo[6.1.0]nonane can be converted by dimethyldioxirane to a ketone.
- L5 ANSWER 23 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
- AN 1996:423571 CAPLUS
- DN 125:104508
- TI Antitumor mechanism of action of a cyclopropyl antiestrogen on human breast cancer cells in culture
- AU Jain, Pramod T.; Pento, J. Thomas; Magarian, Robert A.
- CS Health Sciences Center, University Oklahoma, Oklahoma, OK, 73190, USA
- SO Cancer Chemotherapy and Pharmacology (1996), 38(3), 238-244 CODEN: CCPHDZ; ISSN: 0344-5704
- PB Springer
- DT Journal
- LA English
- Cyclopropyl compound (I) [(Z)-1,1-dichloro-2-[4-[2-AB (dimethylamino) ethoxy]phenyl]-2-(4-methoxyphenyl)-3-phenylcyclopropane] was shown to be a pure antiestrogen in mouse uterine tissue. Antitumor activity was examined by evaluating the influence of I on the proliferation, estrogen receptor (ER) affinity and cell-surface morphol. of ER-pos. and ER-neg. human breast cancer cells in culture. The antiproliferative potency of I was found to be equal to tamoxifen in ER-pos. MCF-7 human breast cancer cells. Further, the antiproliferative activities of I and tamoxifen were reversed by coadministration of estradiol. Accordingly, the antiproliferative activity of I appears to be estrogen-mediated, since it did not influence the growth of either ER-neg. MDA-MB-231 human breast cells or A-549 human lung cancer cells in culture. An ER-dependent mechanism of action is also supported by the specific binding affinity of I for ER in MCF-7 cells. Further, a study of cell surface morphol. using SEM revealed that I reduced the d. and distribution of microvilli (MV) on MCF-7 cells, which was reversed by coadministration of estradiol. I did not alter the cell surface morphol. of ER-neg. MDA-MB-231 cells. In conclusion, I inhibited the growth of ER-pos. MCF-7 cells in an estradiol-reversible manner, and had no effect on either ER-neg. MDA-MB-231 cells or A-549 lung cancer cells. The results of this study confirm an antiestrogenic mechanism of action for I as previously observed in vivo and suggest that I would be effective in the treatment of estrogen-dependent breast cancer or as a prophylactic treatment for women with a high risk of breast cancer development.
- L5 ANSWER 24 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
- AN 1996:395049 CAPLUS
- DN 125:114033
- TI Kinetics of the mediated reduction of gem-dichlorocyclopropanes
- AU Yanilkin, V. V.; Maksimyuk, N. I.; Strunskaya, E. I.; Garifullin, B. M.; Kargin, Yu. M.
- CS Kazan Scientific Cent., Russian Acad. Scis., Kazan, 420083, Russia
- SO Izvestiya Akademii Nauk, Seriya Khimicheskaya (1993), (8),

1407-1410 CODEN: IASKEA

- PB Institut Organicheskoi Khimii im. N. D. Zelinskogo Rossiiskoi Akademii Nauk
- DT Journal
- LA Russian
- The effects of organic electron transfer agents and of Pt(II), Pd(II), Rh(III), Co(II), Ni(II), Cu(II), Cr(III), Mn(II), Ti(III), V(III), Zn(II), and Ag(I) ions on the kinetics of homogeneous reduction of gem-dichlorocyclopropanes are studied. Pt(II), Pd(II), Rh(III), Co(II), and Ni(II) ions accelerate this process; V(III) and Ag(I) ions exert practically no effect; and the rest of the metal ions inhibit the process.
- L5 ANSWER 25 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
- AN 1996:387386 CAPLUS
- DN 125:142196
- TI Photoreaction of homobenzoquinones with amine donors
- AU Moriwaki, Hiroshi; Matsumoto, Takashi; Nagai, Toshikazu; Oshima, Takumi
- CS Fac. Eng., Osaka Univ., Toyonaka, 560, Japan
- SO Journal of the Chemical Society, Perkin Transactions 1: Organic and Bio-Organic Chemistry (1996), (12), 1461-1466
 - CODEN: JCPRB4; ISSN: 0300-922X
- PB Royal Society of Chemistry
- DT Journal
- LA English

GΙ

- The photoreactions of diphenylhomobenzoquinones I (R1 = Me, R2 = H, R3 = AB Br, Me; R1 = H, Me, R2 = R3 = Me) were investigated in the presence of amine donors. The products of these reactions are much dependent on the substituents and the nature of added amines. Irradiation of I (R1 = Me, R2 = H, R3 = Br) with triethylamine (TEA) resulted in ring opening of the fused cyclopropane to give 2-diphenylmethyl-1,4-benzoquinone (II). However, the photoreaction of I (R1 = Me, R2 = H, R3 = Br) with N, N-dimethylaniline (DMA) yielded the 1:1 aminated bicyclic dione III and bis(pdimethylaminophenyl)methane along with II. In contrast, irradiation of 1-Me substituted diphenylhomobenzoquinones I (R3 = Me) with TEA brought about hydrogenation of the C:C double bond to give the bicyclic diones III (R1 = Me, R2 = R4 = H; R1 = R4 = H, R2 = Me; R1 = H, R2 = R4 = Me). photoreaction of I (R1 = R3 = Me, R2 = H; R1 = H, R2 = R3 = Me) DMA provided only the 1:1 aminated bicyclic diones, although trisubstituted I (R1-R3 = Me) remained essentially intact.
- L5 ANSWER 26 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
- AN 1996:364592 CAPLUS
- DN 125:114205
- TI Synthesis of alkenylidenecyclopropanes under phase-transfer and supersonic wave conditions
- AU Chen, Yifei; Isagawa, Kakuzo; Yoshio, Otsuji
- CS Dept. Chem., Shanghai Normal Univ., Shanghai, Peop. Rep. China
- SO Huaxue Tongbao (1995), (12), 36-38
- CODEN: HHTPAU; ISSN: 0441-3776
- PB Kexue
- DT Journal
- LA Chinese

GI

$$\begin{array}{c} \text{Me} \\ \text{Ph} \end{array} c = c = \begin{array}{c} \text{Me} \\ \text{Ph} \end{array}$$

AB Reaction of CHBr3 with α -methylstyrene in CH2Cl2 in the presence of NaOH and triethylbenzylammonium chloride under ultrasonic irradiation gave 98% 1,1-dibromo-2-methyl-2-phenylcyclopropane, which was treated with α-methylstyrene in the presence of Bu4N+HSO4- under ultrasonic irradiation to give 92.6% alkenylidenecyclopropane I.

L5 ANSWER 27 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN

ΔΝ 1996:239125 CAPLUS

DM 124:306769

ΤI Influence of cyclopropyl antiestrogens on the cell cycle kinetics of MCF-7 human breast cancer cells

Jain, Pramod T.; Pento, J. Thomas; Magarian, Robert A. ΑU

CS Health Sciences Center, University Oklahoma, Oklahoma, OK, 73190, USA

Anticancer Research (1995), 15(6B), 2529-32 SO

CODEN: ANTRD4; ISSN: 0250-7005

PΒ Anticancer Research

DT Journal

LA English

Five cyclopropyl compds., previously shown to exhibit pure antiestrogenic AR activity in the mouse uterotropic assay and antiproliferative activity of MCF-7 human breast cancer cells in culture, were examined for their influence on the cell cycle kinetics of MCF-7 cells. The DNA-histogram of a single cell suspension was obtained on Coulter Epics V after fixing the cells in 70 % Et alc. and staining in propidium iodide. Tamoxifen increased the percentage of cells in G1-phase with a concomitant decrease in percentage of cells in S-phase, in an estradiol reversible manner. Cyclopropyl compound 7a ([Z]-1,1-dichloro-2,3-diphenyl-2-(4-(2dimethylamino)ethoxy)phenylcyclopropane, dihydrogen citrate salt) increased the percentage of cells in G1-phase, in an estradiolirreversible manner. 7A and three other compds. decreased the percentage of cells in S-phase and increased percentage of cells in the G2M-phase, in an estradiol-irreversible manner. Of the five cyclopropyl compds. tested, only one had no influence on the cytokinetic parameters, even though this compound was found to exhibit antiproliferative activity on MCF-7 cells equal to that of tamoxifen. In conclusion, all of the cyclopropyl compds., except for one, altered cell cycle parameters of MCF-7 cells in a manner different than that of tamoxifen. Thus, the results of this study indicate that, although these cyclopropyl compds. are antiestrogenic, they produce antiproliferative activity by a distinct mechanism of action in estrogen receptor pos. breast cancer cells.

L5 ANSWER 28 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN

AN 1996:170559 CAPLUS

DN 124:316549

ΤТ Synthesis and chiral separation of some antitumor agents

Singh, Satendra; Meyer, Karen L.; Magarian, Robert A.

CS Department Medicinal Chemistry Pharmaceutics, University Oklahoma Health Sciences Center, Oklahoma City, OK, 73190, USA

SO Bioorganic Chemistry (1996), 24(1), 81-94

CODEN: BOCMBM; ISSN: 0045-2068

PΒ Academic

DTJournal

LA English

ΑU

AR Four Z-isomers of 1,1-dichloro-2,2,3-triarylcyclopropane (DTACs), designed as potent antitumor agents, were synthesized from their appropriately substituted ethenes, which were prepared from the Grignard reaction followed by the dehydration of their intermediate carbinols. The stereospecific addition of dichlorocarbene to the ethenes followed by fractional crystallization afforded (Z)-1,1-dichloro-2-(4-benzyloxyphenyl)-2-(4-methoxy)-3phenylcyclopropane and (Z)-1,1-dichloro-2,3-diphenyl-2-(4methoxyphenyl)cyclopropane. Displacement of the bromo group from the ethoxy side chain intermediates with dimethylamine gave the desired basic side chain compds., (Z)-1,1-dichloro-2,3-diphenyl-2-[4-(2-dimethylaminoethoxy)phenyl]cyclopropane and (Z)-1,1-dichloro-2-[4-(2-dimethylaminoethoxy)phenyl]-2-(4-methoxyphenyl)-3-phenylcyclopropane. While both E- and Z-stereoisomers of the DTACs were isolated using fractional crystallization, only the Z-compds. were resolved on a chiral stationary phase consisting of amylose tris-3,5-dimethylphenyl carbamate coated on silica gel. Complete resolution of the E-compds. was not observed with this system.

- coated on silica gel. Complete resolution of the E-compds. was not observed ANSWER 29 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN L5 1996:154766 CAPLUS AN DN 124:288884 Reaction of 1,1-dihalo-2-phenylcyclopropanes with sodium nitrite in TΙ trifluoroacetic acid Siginova, L. G.; Al'khamdan, Mokhammad; Petrosyan, V. S. AU CS Russia SO Vestnik Moskovskogo Universiteta, Seriya 2: Khimiya (1995), 36(6), 573-7 CODEN: VMUKA5; ISSN: 0579-9384 PB Izdatel'stvo Moskovskogo Universiteta DTJournal LΑ Russian The title reactions gave PhCH(OCOCF3)CH2CX2NO (X = C1, Br), PhCHXCH2CX2NO AB (X = Cl, Br), and 3-halo-5-phenylisoxazoles. ANSWER 30 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN L5 1996:91061 CAPLUS ANDN 124:158637 The binary mediator system consisting of organic electron carrier and TI metal ions in the reactions of electrochemical reduction of bromo- and chloroorganic compounds Yanilkin, V. V.; Maksimyuk, N. I.; Strunskaya, E. I. AU CS Arbuzov Inst. Org. Phys. Chem., Kazan, 420008, Russia Russian Journal of Electrochemistry (Translation of Elektrokhimiya) (SO **1996**), 32(1), 120-6 CODEN: RJELE3; ISSN: 1023-1935 PΒ MAIK Nauka/Interperiodica DT Journal English LΑ The electrochem. reduction of organohalogen compds. involving a double AB mediator system of metal ions and organic electron carrier is studied. The catalytic action of Ni(II), Co(II), Pd(II), Pt(II) and Rh(III) ions on the kinetics of homogeneous reduction of aliphatic, alicyclic, and aromatic bromo- and chloroorg. compds. by radical-anions of organic compds. in aprotic media containing tetraalkylammonium salts as supporting electrolytes is found. all cases, there is a synergistic effect increasing with the increase in concentration of metal ions and with the decrease in efficiency of the organic carrier. By the example of binary mediator reduction involving Ni(II) and Co(II) ions, the reaction is shown to be of the second order with respect to metal ions. L5 ANSWER 31 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN AN 1995:957641 CAPLUS DN 124:175420 The preparation and lithiation of 3,3-diphenyl-1,1,2-tribromocyclopropane TΙ ΑU Li, Gang; Warner, Philip M. CS Dep. Chem., Northeast. Univ., Boston, MA, 02115, USA Tetrahedron Letters (1995), 36(47), 8573-6 SO CODEN: TELEAY; ISSN: 0040-4039
- LA English

 3,3-Diphenyl-1,1,2-tribromocyclopropane (4) was synthesized from benzophenone in three steps in an overall yield of 11.4%. Treatment of 4 with butyllithium in THF at low temps., generated 1-lithio- and 1,2-dilithiocyclopropenes which were characterized by their quenching products.

PB

DТ

Elsevier

Journal

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ANSWER 32 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
L5
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AN1995:867175 CAPLUS

DN 124:116815

Photoinduced electron-transfer reactions of homonaphthoquinones with amine TT and arene donors

ΑU Moriwaki, Hiroshi; Oshima, Takumi; Nagai, Toshikazu

Dep. Applied Chem., Osaka Univ., Toyonaka, 560, Japan CS

Journal of the Chemical Society, Perkin Transactions 1: Organic and SO Bio-Organic Chemistry (1995), (19), 2517-23 CODEN: JCPRB4; ISSN: 0300-922X

Royal Society of Chemistry

PB

DT Journal

LA English

GI

Photoreactions of monoaryl- and diaryl-homonaphthoquinones bearing Me, AB chloro and bromo substituents have been studied in the presence of amine and arene donors. The products of these photolyses depend on the substituents and the identity of the added donors. Irradiation of bromo-substituted diarylhomoquinones I (R1 = R2 = Ph or p-tolyl) with amines such as triethylamine and diethylamine in various aprotic solvents resulted in the formation of (±) - and meso-3,3'-bis(diarylmethylene) -2,2',3,3'-tetrahydro-2,2'-bi-1,4-naphthoguinones (2) via the dimerization of intermediary allyl radicals arising from bromide release accompanied by ring-opening of the cyclpropane ring. Besides dimer 2, a 1:1 amine adduct II was also obtained with N, N-dimethylaniline as donor. However, methyland chloro-substituted homoquinones remained intact due to the poor leaving ability of these substituents. A similar reaction of bromo-substituted methylphenylhomoquinones I (R1 = Me, R2 = Ph or R1 = Ph, R2 = Me) gave 5-hydroxy-3-phenylnaphtho[1,2-b]furan via $2-(\alpha-phenylvinyl)-1,4-naphthoquinone.$ In contrast, photoreactions of I (R1 = R2 = Ph) in the presence of arene donors, naphthalene and methoxy-substituted benzenes, gave no dimeric product but instead gave photoisomerized 2-bromo-3-diphenylmethylene-2,3-dihydronaphthoquinone (4b) and its photocyclized xanthylium salt (7). This reaction does not occur in nonpolar solvents. In the case of xanthene as donor, the dimer 2 was again formed in addition to 4b and 7. These reaction features were interpreted in terms of a difference between proton donating ability of the donor cation radicals.

- L5 ANSWER 33 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
- ΑN 1995:834681 CAPLUS
- DN 124:29281
- TI Coupling reactions. Part 15. The reaction of 1-halo-1-lithiocyclopropanes with CuCl2: competition between 'carbene dimerization' and oxidative
- Borer, Markus; Loosli, Thomas; Minger, Andrea; Neuenschwander, Markus; ΑU Engel, Peter
- Institut Organische Chemie, Universitaet Bern, Bern, CH-3012, Switz. CS
- SO Helvetica Chimica Acta (1995), 78(5), 1311-24
 - CODEN: HCACAV; ISSN: 0018-019X
- PB Verlag Helvetica Chimica Acta
- DТ Journal
- LA German
- os CASREACT 124:29281
- 2-Phenyl- and 2-phenylthio-1-chloro-1-lithiocyclopropanes reacted at low AB

temperature with CuCl2 to give diastereoisomeric mixts. of bi(cyclopropyls) as oxidative-coupling products and of bi(cyclopropylidenes) as carbene dimers. The relative amount of the latter increased ≤70% with CuCl2 concentration and reaction time. Diastereoselectivity of the reaction was low. The conformational behavior of 1,1'-dichloro-1,1'-bi(cyclopropyls) is discussed. 1-Bromo-1-lithiocyclopropanes gave carbene dimers and no coupling products. The only exception was 1-bromo-1-lithio-2-phenylcyclopropane which gave some percentage of coupling products besides carbene dimers.

- L5 ANSWER 34 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
- AN 1995:834669 CAPLUS
- DN 124:55392
- TI Coupling reactions. Part 14. Copper(II)-chloride catalyzed 'carbene dimerization' of 1-halo-1-lithiocyclopropanes. A simple route to bi(cyclopropylidenes)
- AU Loosli, Thomas; Borer, Markus; Kulakowska, Iga; Minger, Andrea; Neuenschwander, Markus; Engel, Peter
- CS Inst. Org. Chem., Univ. Bern, Bern, CH-3012, Switz.
- SO Helvetica Chimica Acta (1995), 78(5), 1144-65
 - CODEN: HCACAV; ISSN: 0018-019X
- PB Verlag Helvetica Chimica Acta
- DT Journal
- LA English
- OS CASREACT 124:55392
- AB A series of bi(cyclopropylidenes) was prepared in a simple one-pot reaction by halo-lithio exchange between 2-substituted 1,1-dibromocyclopropanes and BuLi followed by treatment with CuCl2 (20-85% yield). The yields depended strongly on reaction parameters. Cross-couplings between different carbenoids were possible.
- L5 ANSWER 35 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
- AN 1995:794621 CAPLUS
- DN 123:339239
- TI Drastic effects of dioxygen on the selectivity of reduction by LiAlH4.

 Milder conditions made possible by strictly anaerobic conditions
- AU Peralez, Eric; Negrel, Jean-Claude; Chanon, Michel
- CS Faculte Sciences St. Jerome, Universite Aix-Marseille III, Marseille, 13013, Fr.
- SO Tetrahedron Letters (1995), 36(36), 6457-60 CODEN: TELEAY; ISSN: 0040-4039
- PB Elsevier
- DT Journal
- LA English
- OS CASREACT 123:339239
- AB Reduction of the gem-disubstituted cyclopropane 1-bromo-2,2-diphenylcyclopropanecarboxylic acid with LiAlH4 yields different results under strictly anaerobic conditions and loosely anaerobic ones. Under strictly anaerobic conditions, (+)-1-bromo-2,2-diphenylcyclopropanemethanol was quant. reduced to 2,2-diphenylcyclopropanemethanol with complete racemization. These observations are explained by a radical chain mechanism. They open the way to redns. by LiAlH4 under mild conditions.
- L5 ANSWER 36 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
- AN 1995:594381 CAPLUS
- DN 123:198417
- TI Gem-dichlorocyclopropanes as antitumor agents
- IN Magarian, Robert A.; Pento, Joseph T.; Griffin, May T.
- PA Research Corporation Technologies, Inc., USA
- SO U.S., 22 pp. Cont.-in-part of U.S. Ser. No. 812,246, abandoned. CODEN: USXXAM
- DT Patent
- LA English
- FAN.CNT 7

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
ΡI	US 5397802	Α	19950314	US 1993-20922	19930222 <
	US 4879315	A	19891107	US 1987-98945	19870921 <

US 5098903	A	19920324	US 1989-432564	19891106 <
US 5663207	A	19970902	US 1995-376961	19950120 <
US 5658927	Α	19970819	US 1995-480212	19950607 <
US 5658914	Α	19970819	US 1995-480215	19950607 <
US 5658951	Α	19970819	US 1995-487717	19950607 <
US 1980-128040	B2	19800307		
US 1980-166255	B2	19800707		
US 1982-363429	B2	19820330		
US 1987-98945	A2	19870921		
US 1989-432564	A2	19891106		
US 1991-812246	B2	19911219		
US 1993-20922	A1	19930222		
US 1995-376961	A2	19950120		
MARPAT 123:198417				
	US 5663207 US 5658927 US 5658914 US 5658951 US 1980-128040 US 1980-166255 US 1982-363429 US 1987-98945 US 1989-432564 US 1991-812246 US 1993-20922 US 1995-376961	US 5663207 A US 5658927 A US 5658914 A US 5658951 A US 1980-128040 B2 US 1980-166255 B2 US 1982-363429 B2 US 1987-98945 A2 US 1989-432564 A2 US 1991-812246 B2 US 1993-20922 A1 US 1995-376961 A2	US 5663207 A 19970902 US 5658927 A 19970819 US 5658914 A 19970819 US 5658951 A 19970819 US 1980-128040 B2 19800307 US 1980-166255 B2 19800707 US 1982-363429 B2 19820330 US 1987-98945 A2 19870921 US 1989-432564 A2 1987106 US 1991-812246 B2 19911219 US 1993-20922 A1 19930222 US 1995-376961 A2 19950120	US 5663207 A 19970902 US 1995-376961 US 5658927 A 19970819 US 1995-480212 US 5658914 A 19970819 US 1995-480215 US 5658951 A 19970819 US 1995-487717 US 1980-128040 B2 19800307 US 1980-166255 B2 19800707 US 1982-363429 B2 19820330 US 1987-98945 A2 19870921 US 1989-432564 A2 1987106 US 1991-812246 B2 19911219 US 1993-20922 A1 19930222 US 1995-376961 A2 19950120

The present invention relates to gem-dichlorocyclopropanes I or any pharmaceutically acceptable salt thereof, in which X is a halogen atom; R1 is a hydrogen; R2 is a hydroxyphenyl; and R3 is a cyclopentyl group having the first position carbon and the fifth position carbon bonded to the same carbon of the cyclopropane wherein the R4 group is absent. I (Analog II derivs.) demonstrate antiproliferative activity toward MCF-7 cells, in vitro and are generally not reversed by estradiol or having intrinsic estrogenicity (except the hydroxyphenyl derivative II). Thus, e.g., demethylation of 1,1-dichloro-2,2-bis-(p-methoxyphenyl)spiro[2.5]octane (preparation given) afforded 54% II which displayed estrogen receptor binding affinity of 0.62 % (relative to that of estradiol = 100%) and inhibition of MCF-7 human breast cancer cell of 21.3%.

TT

L5 ANSWER 37 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN

AN 1995:560783 CAPLUS

Ι

DN 123:227499

TI Thermal decomposition of homoquinones. [Erratum to document cited in CA123:169111]

AU Oshima, Takumi; Tamada, Kazushi; Nagai, Toshikazu

CS Inst. Chem., Osaka Univ., Osaka, 560, Japan

SO Journal of the Chemical Society, Perkin Transactions 1: Organic and Bio-Organic Chemistry (1995), (9), 1199
CODEN: JCPRB4; ISSN: 0300-922X

Royal Society of Chemistry

DT Journal

PB

LA English

AB The errors were not reflected in the abstract or the index entries.

L5 ANSWER 38 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN

AN 1995:328082 CAPLUS

DN 123:9080

TI Reactivity of the acids of trivalent phosphorus and their derivatives.

Part III. The P-O- ions in reaction with activated alkyl bromides. Attack
on bromine vs. electron transfer

AU Dembkowski, Leszek; Rachon, Janusz

CS Department of Organic Chemistry, Technical University of Gdansk, Gdansk,

```
SO Phosphorus, Sulfur and Silicon and the Related Elements (1994),
91(1-4), 251-62
CODEN: PSSLEC; ISSN: 1042-6507

PB Gordon & Breach

DT Journal

LA English

OS CASREACT 123:9080

GI

Ph
R

Ph
R

I
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The mechanism of reductive debromination in the course of the reaction of sodium dialkyl (diaryl) phosphites as well as the sodium salt of dibenzylphosphine oxide with activated alkyl bromides in THF has been investigated. Probable mechanisms namely, SET and X-philic substitution are discussed. The cyclopropyl system was chosen for the study of this reaction. Thus, bromocyclopropanes I [R = Br, CO2Me, CONH2, cyano, P(O) (OMe) 2, R1 = Br] gave I (R1 = H) upon debromination. The results of the carried out expts. (unrearranged products, no influence of light) suggests that the cyclopropyl radical intermediate (if it is formed) does not participate in the product-determining step of the reductive debromination under the action of the >P-O- ions.

L5 ANSWER 39 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN

AN 1995:301276 CAPLUS

80-952, Pol.

DN 122:105104

TI Kinetics of homogeneous reduction of bromo- and chloroorganic compounds by radical anions of anthracene in the presence of NiII and CoII ions

AU Yanilkin, V. V.; Maximyuk, N. I.; Karqin, Yu. M.

CS A. E. Arbuzov Inst. Org. Phys. Chem., Kazan' Sci. Cent. Russian Acad. Sci., Kazan', 420083, Russia

SO Izvestiya Akademii Nauk, Seriya Khimicheskaya (1994), (6), 1022-4

CODEN: IASKEA

PB Institut Organicheskoi Khimii im. N. D. Zelinskogo Rossiiskoi Akademii Nauk

DT Journal

LA Russian

AB The effect of NiII and CoII ions on the kinetics of homogeneous reduction of some aromatic, aliphatic and cyclic bromo- and chloroorg. compds. by anthracene radical anions has been studied by polarog. The catalytic activity of the metal ions increases with decreasing reducibility of the halogenated substrates.

L5 ANSWER 40 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN

AN 1995:237498 CAPLUS

DN 123:169111

TI Thermal decomposition of homoguinones

AU Oshima, Takumi; Tamada, Kazushi; Nagai, Toshikazu

CS Inst. Chem., Osaka Univ., Osaka, 560, Japan

SO Journal of the Chemical Society, Perkin Transactions 1: Organic and Bio-Organic Chemistry (1994), (22), 3325-33
CODEN: JCPRB4; ISSN: 0300-922X

PB Royal Society of Chemistry

DT Journal

LA English

GΙ

- Thermolysis of diphenyl- and biphenyl-2,2'-diyl-substituted AB homobenzoquinones I (X1 = H, Me, Br, Cl; X2 = H, Br; X3 = Me, Cl, Br; R1 = R2 = Ph; R1R2 = biphenyl-2,2'-diyl) and homonaphthoquinones II (same X3, R1, R2) was investigated at 100°C. The biphenyl-2,2'diylhomoquinones I and II with halo substituents were thermolyzed to 2-(9-halofluoren-9-yl)-1,4-benzoquinones and -1,4-naphthoquinones, resp., via a cyclopropane ring-opening reaction. The diphenylhomoquinones were thermally less labile so that only ones bearing a bromo substituent underwent a cyclopropane ring-opening to afford a different type of product, 2-bromo-3-diphenylmethylene-2,3-dihydro-1,4-benzoquinones and -1,4-naphthoquinone, resp. The product change was attributed to the steric requirement of the intermediary allyl cations. Some reactions of the products were investigated on the basis of Frontier MO considerations. The different behavior of the bromoquinones 3c-e and 10 was interpreted on the basis of Frontier MO considerations.
- L5 ANSWER 41 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
- AN 1995:127411 CAPLUS
- DN 122:80732
- TI Synthesis of Z-1,1-dichloro-2-[4-(2-dimethylaminoethoxy)phenyl]-2-(4-hydroxyphenyl)-3-phenylcyclopropane and Z-1,1-dichloro-2-[4-(2-dimethylaminoethoxy)phenyl]-2-(4-chlorophenyl)-3-phenylcyclopropane
- AU Singh, Satendra; Magarian, Robert A.
- CS College of Pharmacy, University of Oklahoma, Oklahoma City, OK, 73190, USA
- SO Chemistry Letters (1994), (10), 1821-4
- CODEN: CMLTAG; ISSN: 0366-7022
- DT Journal
- LA English

GΙ

 $Me_2NCH_2CH_2O$

- AB The synthesis of title compds. I (R = HO, Cl) is described. The key steps in the synthesis are the preparation of the pure Z-ethene, the stereospecific addition of dichlorocarbene, amino-dehalogenation and deprotection of the phenol. Heptafluorotolyl protecting group is used in the synthesis of pure Z-ethene which is stable under basic heterogeneous cyclopropanation reaction conditions.
- L5 ANSWER 42 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
- AN 1994:604530 CAPLUS
- DN 121:204530
- TI Reactivity of the acids of trivalent phosphorus and their derivatives.

 Part I. Reductive debromination in the reactions of the P-O- ions with

 2-bromo esters
- AU Dembkowski, Leszek; Rachon, Janusz

CS Dep. Org. Chem., Tech. Univ. Gdansk, Gdansk, 80-952, Pol.

SO Phosphorus, Sulfur and Silicon and the Related Elements (1994), 88(1-4), 27-37

CODEN: PSSLEC; ISSN: 1042-6507

DT Journal

LA English

AB The reaction of α -bromo carboxylates with sodium dialkyl or diaryl phosphites and the sodium salt of dibenzylphosphine oxide afforded debromination products in THF or alcs. as the solvents. Probable mechanisms are discussed.

L5 ANSWER 43 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN

AN 1994:579451 CAPLUS

DN 121:179451

TI Photoisomerization of bromonaphthoquinone-fused diphenylcyclopropane into xanthylium salt in the presence of arene donors

AU Moriwaki, Hiroshi; Oshima, Takumi; Nagai, Toshikazu

CS Coll. Gen. Education, Osaka Univ., Toyonaka, 560, Japan

SO Journal of the Chemical Society, Chemical Communications (1994), (14), 1681-2

CODEN: JCCCAT; ISSN: 0022-4936

DT Journal

LA English

GI

AB Irradiation of naphthoquinone-fused diphenylcyclopropane I (X = Br) in the presence of naphthalene, dimethoxybenzene or triphenylamine gave xanthylium salt II [benzo[c]xanthylium] via an intramol. cyclization of intermediary 2-bromo-3-diphenylemthylene-2,3-dihydronaphthoquinone.

Naphthoquinone-fused diphenylcyclopropane I (X = Cl, Me) did not undergo a photochem. reaction.

L5 ANSWER 44 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN

AN 1994:569770 CAPLUS

DN 121:169770

TI A comparison of the antitumor activity of two triarylcyclopropyl antiestrogens on human breast cancer cells in culture

AU Jain, Pramod T.; Pento, J. Thomas; Magarian, Robert A.

CS College Pharmacy, Univ. Oklahoma, Oklahoma City, OK, 73190, USA

Anti-Cancer Drugs (1994), 5(4), 429-36 CODEN: ANTDEV; ISSN: 0959-4973

DT Journal

LA English

GI

SO

AB (E) - and (Z) -1,4-dichloro-2-[4-(benzyloxy)phenyl]-2,3-bis(4-methoxyphenyl) cyclopropane (I) and (Z)-1,1-dichloro-2-[4-(benzyloxy)phenyl]-2-(4methoxyphenyl)-3-phenylcyclopropane (II) are two members of a novel series of triarylcyclopropyl compds. which have been shown to be pure antiestrogens. In the present study, the antiproliferative activity of I and II was examined on estrogen receptor (ER)-pos. MCF-7 and ER-neg. MDA-MB-231 human breast cancer cells and A-549 human lung cancer cells. Compound I inhibited the growth of MCF-7 cells in a dose-related manner over a concentration range of 10-13 to 10-5M while compound II inhibited MCF-7 cell growth in a dose-related manner over a concentration range of 10-9 to 10-5 M. Further, neither compound altered the growth of MDA-MB-231 or A-549 cells. Coadministration of estradiol reversed the antiproliferative activity of I but not II on MCF-7 cells. Both compds. bound specifically to ER in MCF-7 cells; however, the relative binding activity of I was five times greater than estradiol and 5000 time greater than II. The influence of I and II on the cell surface morphol. of MCF-7 and MDA-MB-231 cell was studied using SEM. Both compds., at a concentration of 10-6 M, réduced the d. of microvilli on MCF-7 cells, which was reversed by coadministration of estradiol (10-8 M). These compds. did not alter the cell surface morphol. of ER-neg. MDA-MB-231 cells. In conclusion, the results of this study indicate that compound I is more potent than II as an inhibitor of breast cancer cell proliferation and suggest that a polar methoxy group on the β Ph ring of compound I contributes to ER binding and ER-mediated antitumor activity. Further, these results suggest that one or both of these compds. may be highly effective in the treatment of estrogen-dependent breast cancer.

Ι

L5 ANSWER 45 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
AN 1994:557214 CAPLUS
DN 121:157214
TI (Z)-1,1-dichloro-2-(4-benzyloxyphenyl)-2,3-bis(4-

(Z)-1,1-dichloro-2-(4-benzyloxyphenyl)-2,3-bis(4-methoxyphenyl)cyclopropane: the synthesis and enantiomeric separation of an antitumor agent

AU Meyer, Karen L.; Magarian, Robert A.

CS Coll. Pharm., Univ. Oklahoma, Oklahoma City, OK, 73190, USA

Chirality (1994), 6(1), 41-5 CODEN: CHRLEP; ISSN: 0899-0042

DT Journal LA English

OS CASREACT 121:157214

GI

AB

SO

II

methoxyphenyl)cyclopropane (I), a potential antitumor agent designed to treat breast cancer, was prepared in three steps. A stereospecific palladium-catalyzed cross coupling reaction which provided the intermediate (Z)-triaryl alkene II was a crucial step in the synthesis. Makosza phase transfer reaction on II gave the enantiomeric (Z)-dichlorocyclopropane derivs. I which were resolved by semipreparative HPLC on a chiral stationary phase consisting of amylose tris-3,5-dimethylphenylcarbamate coated on silica gel.

- ANSWER 46 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN L5 AN 1994:556910 CAPLUS DN 121:156910 Photoinduced reductive cleavage of diarylcyclopropanes fused with ΤI bromonaphthoquinone in the presence of amines ΑU Moriwaki, Hiroshi; Oshima, Takumi; Nagai, Toshikazu CS Coll. Gen. Educ., Osaka Univ., Toyonaka, 560, Japan SO Journal of the Chemical Society, Chemical Communications (1994), CODEN: JCCCAT; ISSN: 0022-4936 DTJournal
- * STRUCTURE DIAGRAM TOO LARGE FOR DISPLAY AVAILABLE VIA OFFLINE PRINT *
- AB Irradiation of the title diarylcyclopropanes I-II in the presence of amines results in the dimerization of the intermediary allyl radicals III-IV, formed by the reductive cleavage of the cyclopropane ring.
- L5 ANSWER 47 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
- AN 1994:322895 CAPLUS
- DN 120:322895

English

CASREACT 121:156910

LA

os

GI

- TI Nickel-Catalyzed Cross Coupling of Cyclopropyl Grignard Reagents with Benzylic Dithioacetals. Regioselective Ring Opening of Cyclopropylcarbinyl Organometallic Intermediates. Novel Synthesis of Substituted Dienes
- AU Yu, Chun Chi; Ng, Dennis K. P.; Chen, Bi-Ling; Luh, Tien-Yau
- CS Department of Chemistry, National Taiwan University, Taipei, 106, Taiwan
- SO Organometallics (1994), 13(4), 1487-97 CODEN: ORGND7; ISSN: 0276-7333
- DT Journal
- LA English
- OS CASREACT 120:322895
- The reactions of various cyclopropylmagnesium bromides with benzylic dithioacetals afforded the corresponding substituted conjugate dienes in good yields. Thus, for example, NiCl2(PPh3)2-catalyzed reaction of 1-naphthaldehyde 1,2-ethanedithiol dithioacetal with cyclopropylmagnesium bromide afforded 66% 1-Cl0H7CH:CHCH:CH2. These reactions can be considered as using cyclopropyl anion as an allyl anion synthon. The reaction shows high regio- and stereoselectivity to give E isomers predominantly, if not exclusively. The nature of the substituent(s) in the ring-opening process in the (cyclopropylcarbinyl)nickel intermediate has been investigated in detail. An aryl or vinyl substituent gives regioselective ring opening at the more substituted carbon-carbon bond, an alkyl substituent being unselective. β -Heteroatom elimination in these nickel-catalyzed cross-coupling reactions has been used for regioselective synthesis of 1,4-dienes.
- L5 ANSWER 48 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
- AN 1994:322414 CAPLUS
- DN 120:322414
- TI Molecular Structures and Conformational Studies of Triarylcyclopropyl and Related Nonsteroidal Anti-Estrogens
- AU Hossain, M. Bilayet; van der Helm, Dick; Schmitz, Francis J.; Pordesimo, Eva O.; Magarian, Robert A.; Meyer, Karen L.; Overacre, Lynette B.; Day, Billy W.

CS Department of Chemistry and Biochemistry, University of Oklahoma, Norman, OK, 73019, USA

SO Journal of Medicinal Chemistry (1994), 37(11), 1670-83 CODEN: JMCMAR; ISSN: 0022-2623

DT Journal LA English

GΙ

Mol. structures and conformational characteristics of a series of AB 1,1-dichloro-2,2,3-triarylcyclopropanes I (R, R1 = Ph, 4-MeOC6H4; R2 = Me, PhCH2, Me2NCH2CH2) (DTACs), which were reported previously as distinctly antiestrogenic and inhibitors of the estrogen-receptor-pos. MCF-7 human breast cancer cells in culture, are reported. In addition, structural and conformational features of I were compared to the first-known nonsteroidal anti-estrogen, MER25, and the clin. useful anti-estrogen tamoxifen. mol. structures of I were determined by X-ray diffraction. Crystallog. structures show that I have nearly the same relative conformation for the three aryl rings (designated as a "nonpropeller" conformation), in contrast to the observed "propeller" conformation for the three rings in all known triarylethylenes. Systematic conformational searches were performed to find the conformational preferences of I, MER25, and tamoxifen using idealized model compds. built from their resp. crystal structure. Energy-minimization and conformational-search studies demonstrated that all I have a common, single global min. energy conformer for their central core containing the dichlorotriarylcyclopropyl system, which is similar to that found in their crystal structures. Conformational search of MER25 showed that it can assume a number of low-energy conformers of which 2 [1 anti (A1), and 1 gauche (G1A)], have about the same energy. The anti conformation is similar to the one observed in its crystal structure and resembles the estrogenic E-isomer of tamoxifen, while the lowest energy gauche conformer of MER25 resembles more closely the antiestrogenic Z-isomer of tamoxifen. NMR of MER25 showed that the mol. exists predominantly in the anti conformation in solution A comparative review of the structural features and bioactivities of tamoxifen, I, and MER25 provides a possible explanation for their low estrogen receptor binding affinity which is common to these compds. together with their antiestrogenic activity.

L5 ANSWER 49 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN

AN 1994:298159 CAPLUS

DN 120:298159

TI Hydrogenolysis of gem-diphenylcyclopropanes fused with trihalogenated guinones

AU Oshima, Takumi; Nakajima, Yuichi; Nagai, Toshikazu

Coll. Gen. Educat., Osaka Univ., Toyonaka, 560, Japan

Chemistry Letters (1993), (11), 1977-80

CODEN: CMLTAG; ISSN: 0366-7022

DT Journal

LA English

OS CASREACT 120:298159

GI

CS

SO

- AB Palladium-catalyzed hydrogenolysis of gem-diphenylcyclopropanes fused with trihalogenobenzoquinones, e.g., I, gave diphenylmethylhydroquinones, e.g., II. Water took part in the reaction to yield $\alpha-$ hydroxydiphenylmethyl- and benzoylhydroquinones. The selective ring-cleavage was interpreted in terms of the $\pi-$ conjugative interaction of cyclopropane.
- L5 ANSWER 50 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN

AN 1994:69769 CAPLUS

DN 120:69769

- TI The influence of a novel cyclopropyl antiestrogen (compound 7a) on human breast cancer cells in culture
- AU Jain, Pramod T.; Pento, J. Thomas; Magarian, Robert A.
- CS Coll. Pharm., Univ. Oklahoma, Oklahoma City, OK, 73190, USA
- SO Breast Cancer Research and Treatment (1993), 25(3), 225-33
 - CODEN: BCTRD6; ISSN: 0167-6806
- DT Journal
- LA English
- Compound 7a ([Z]-1,1-dichloro-2,3-diphenyl-2-(4-(2-AB dimethylamino)ethoxy)phenyl)cyclopropane, dihydrogen citrate salt is a novel cyclopropyl antiestrogen which was shown to be an estrogen antagonist without estrogen agonist activity. The antiproliferative activity of 7a was examined on estrogen receptor (ER) pos. MCF-7 and ER-neq. MDA-MB-231 human breast cancer cells and A-549 human lung cancer cells. Compound 7a inhibited the growth of MCF-7 cells in a dose-related manner over a concentration range of 10-9 to 10-5M, but did not alter the growth of MDA-MB-231 or A-549 cells. The antiproliferative activity of 7a (10-7M) on MCF-7 cells was reversed by co-administration of estradiol (10-8M). ER-dependent mechanism of action is also supported by the specific ER binding of 7a in MCF-7 cells observed in this study. A study of cell surface morphol. using SEM revealed that compound 7a at 10-6M reduced the length and d. of microvilli (MV) on MCF-7 cells, which was reversed by co-administration of estradiol (10-8M). Compound 7a did not alter the cell surface morphol. of ER-neg. MDA-MB-231 cells. In conclusion, 7a inhibited the growth of ER-pos. MCF-7 cells in an estradiol-reversible manner, and had no effect on ER-neg. MDA-MB-231 cells or A-549 lung cancer cells. results of this study support the antiestrogenic action of 7a previously observed in vivo and suggest that 7a may be highly effective in the treatment of estrogen-dependent breast cancer and/or in the prophylactic treatment of women with a high risk of breast cancer development.
- L5 ANSWER 51 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
- AN 1994:30430 CAPLUS
- DN 120:30430
- TI Generation, reactions, direct observation, and kinetics of decafluorodiphenylcarbene
- AU Tomioka, Hideo; Mizutani, Kenzoh; Matsumoto, Kenji; Hirai, Katsuyuki
- CS Fac. Eng., Mie Univ., Tsu, 514, Japan
- SO Journal of Organic Chemistry (1993), 58(25), 7128-34 CODEN: JOCEAH; ISSN: 0022-3263
- DT Journal
- LA English
- AB Bis (pentafluorophenyl) diazomethane (1a) was prepared, and reactivities of perfluorodiphenylcarbene (2a) generated by photolysis of la were investigated not only in terms of product anal. but also by using matrix isolation spectroscopy as well as laser flash photolysis techniques. Product distributions observed in the reactions of 2a in benzene, cyclohexane, and trans-1,2-dichloroethylene suggested that 2a reacted with those substrates with moderate reactivities toward carbene mostly in its

singlet state presumably owing to the increased electrophilicity induced by fluorine substituents while the reaction with the alkane C-H bonds in concerted fashion was retarded partly due to steric effect in the singlet state which thus decayed to the triplet states that underwent predominantly H atom abstraction forming tetraarylethane. Photolysis of 1a in Ar matrix at 10 K produced 2a which was observed by IR and UV and shown to react with doped O2 to produce ultimately perfluorobenzoate by way of the carbonyl oxide and dioxirane, both intermediates being characterized by IR and UV/vis spectroscopy. Laser flash photolysis of 1a in cyclohexane solution produced a transient absorption (λ = 320 nm) due to bis(pentafluorophenyl)methyl radical (14a) obviously produced by H atom abstraction of the triplet 2a, which was trapped by oxygen to generate the carbonyl oxide, and also by 1,4-cyclohexadiene to form the Me radical (14a). The lifetime of the triplet 2a was estimated to be .apprx.1 μ s.

- L5 ANSWER 52 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
- AN 1993:538584 CAPLUS
- DN 119:138584
- TI The nature of electron transfer from metal surfaces to the carbon-halogen bond
- AU Walborsky, H. M.; Hamdouchi, C.
- CS Dittmer Lab. Chem., Florida State Univ., Tallahassee, FL, 32306, USA
- SO Journal of the American Chemical Society (1993), 115(14), 6406-8 CODEN: JACSAT; ISSN: 0002-7863
- DT Journal
- LA English
- AB Electrochem. reduction of organic halides at a glassy carbon electrode is reported. Electron transfer and cleavage of the carbon-halogen bond for the substrates studied are concerted.
- L5 ANSWER 53 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
- AN 1993:494883 CAPLUS
- DN 119:94883
- TI Chiroptical properties of the benzene chromophore in substituted 1,1-diphenylcyclopropanes
- AU Gawronski, J.; Gawronska, K.; Radocki, D.; Walborsky, H. M.
- CS Dep. Chem., A. Mickiewicz Univ., Poznan, 60-780, Pol.
- SO Tetrahedron: Asymmetry (1993), 4(3), 383-92 CODEN: TASYE3; ISSN: 0957-4166
- DT Journal
- LA English
- AB The CD spectra of 29 derivs. of 1,1-diphenylcyclopropane of known absolute configuration have been measured. The min.-energy perpendicular conformation of these mols. follows from MMX calcns. as well as from available x-ray data. A contribution of substituents X and Y in the 2-position of the cyclopropane ring to the rotatory strength of the Ph chromophores is evaluated, and a simple rule relating the size and donor character of the substituent to the sign of the 1Lb and 1La Cotton effects is proposed.
- L5 ANSWER 54 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
- AN 1993:408372 CAPLUS
- DN 119:8372
- TI Cyclopropylidene dianion equivalent. Preparation of 1,1-dilithio-2,2-diphenylcyclopropane
- AU Oku, Akira; Ose, Yasuyoshi; Kamada, Tohru; Yoshida, Tomohiro
- CS Dep. Chem. Mater. Technol., Kyoto Inst. Technol., Kyoto, 606, Japan
- SO Chemistry Letters (1993), (3), 573-6 CODEN: CMLTAG; ISSN: 0366-7022
- DT Journal
- LA English
- AB The title compound was prepared by the treatment of the corresponding 1,1-dibromocyclopropane with lithium naphthalene radical anion (Li-C10H8). Trapping of the dilithio compound by chlorotrimethylsilane provided evidence for its highly basic profile which can compete with silylation.
- L5 ANSWER 55 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
- AN 1993:213135 CAPLUS
- DN 118:213135

TI Mechanism of organocalcium reagent formation

AU Walborsky, H. M.; Hamdouchi, C.

CS Dittmer Lab. Chem., Florida State Univ., Tallahassee, FL, 32306, USA

SO Journal of Organic Chemistry (1993), 58(5), 1187-93

CODEN: JOCEAH; ISSN: 0022-3263

- DT Journal
- LA English
- AB The stereochem. of the reaction of (S)-(+)-1-bromo- and
 - (S)-(+)-1-chloro-1-methyl-2,2-diphenylcyclopropane and
 - (S)-(+)-1-bromo-1-(methoxymethyl)-2,2-diphenylcyclopropane with

calcium-aromatic complexes is reported as is reaction with a radical clock, 6-chloro-6-methyl-1-heptene. Evidence is presented which indicates that these reactions occur by a single electron transfer to yield free radicals

as intermediates. The reduction of a number of these substrates with solns. of calcium dissolved in liquid ammonia is also reported. Metallic bronze Ca(NH3)6 in THF at -30 ° behaves as a solid surface in its reaction

with alkyl halides.

- L5 ANSWER 56 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
- AN 1993;212827 CAPLUS
- DN 118:212827
- TI Xanthylium salts from thermolysis of diphenylcyclopropanes fused with bromo-substituted 1,4-benzoquinones
- AU Oshima, T.; Nagai, T.
- CS Coll. Gen. Educ., Osaka Univ., Toyonaka, 560, Japan
- SO Tetrahedron Letters (1993), 34(4), 649-52
 - CODEN: TELEAY; ISSN: 0040-4039
- DT Journal
- LA English
- OS CASREACT 118:212827

GI

- AB Thermolysis of diphenylcyclopropanes, e.g., I, fused with bromo-substituted 1,4-benzoquinones resulted in the formation of xanthylium salts,e.g., II, via ring opening accompanied by 6π electrocyclization.
- L5 ANSWER 57 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
- AN 1993:123834 CAPLUS
- DN 118:123834
- TI Chiral carbenoids: their formation and reactions
- AU Topolski, M.; Duraisamy, M.; Rachon, J.; Gawronski, J.; Gawronska, K.; Goedken, V.; Walborsky, H. M.
- CS Dittmer Lab. Chem., Florida State Univ., Tallahassee, FL, 32306, USA
- SO Journal of Organic Chemistry (1993), 58(3), 546-55 CODEN: JOCEAH; ISSN: 0022-3263
- DT Journal
- LA English
- AB Carbenoids, generated by metalation or halogen-metal exchange reactions, have been prepared from chiral vinyl and cyclopropyl halides. The reactivity and stereochem. observed in the reaction of these carbenoids has been interpreted as being due to metal-assisted ionization.
- L5 ANSWER 58 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
- AN 1993:59143 CAPLUS
- DN 118:59143
- TI Role of nickel(II) and cobalt(II) ions in the mediated reduction of gem-dichlorocyclopropanes

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AU Yanilkin, V. V.; Maksimyuk, N. I.; Gritsenko, E. I.; Kargin, Yu. M.; Garifullin, B. M.
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CS A. E. Arbuzov Inst. Org. Phys. Chem., Kazan, 420083, Russia

SO Izvestiya Akademi Nauk, Seriya Khimicheskaya (1992), (2), 292-8 CODEN: IASKEA; ISSN: 1026-3500

DT Journal

LA Russian

OS CASREACT 118:59143

The Co(II) and Ni(II) effect on the kinetics of homogeneous reduction of the title compds. with anthracene anion radicals has been studied. The Co(II) and Ni(II) ions were shown to accelerate this process. The observed effect depends on the nature and concentration of metal ion and on the type of the title cyclopropane. Two mechanisms are discussed, consisting in homogeneous reduction with anthracene anion radicals of metal ions to form the more efficient reducing mono- and zero-valence metals, and also in activation of the dichlorocyclopropane mol. via prior coordination with metal ion.

L5 ANSWER 59 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN

AN 1993:6410 CAPLUS

DN 118:6410

TI Substituent effects on the structure of spiropentane

AU Irngartinger, Hermann; Gries, Stefan; Klaus, Philip; Gleiter, Rolf

Org.-Chem. Inst., Univ. Heidelberg, Heidelberg, D-6900, Germany

Chemische Berichte (1992), 125(11), 2503-12

CODEN: CHBEAM; ISSN: 0009-2940

DT Journal

LA German

CS

SO

GI

$$R^1$$
 $C1$ $C1$ $C1$ $C1$ $C1$ $C1$

In order to investigate the influence of substituents on the bond lengths of the spiropentane framework, the mol. structures of the spiropentane derivs. I (R = Bz, R1, R2 = H, R3 = Ph; R, R1 = Ph, R2 = H, R3 = CO2H; R, R1 = Ph, R2, R3 = Cl, F) and II-IV have been determined by x-ray anal. The π acceptor substituents (Bz, CO2R, Ph) shorten the distal bond of the substituted three-membered ring by δ - 0.02 Å. The vicinal bonds are lengthened by $\delta/2$. The π donor- σ acceptor groups have the opposite effect [δ (Cl2) = 0.019, δ (F2) = 0.056 Å]. The influence of several substituents is additive. The longer peripheral bond [1.530(14) Å] is varied to the same degree as the shorter central bond [1.482(9) Å]. The second three-membered ring of the spiropentane system is not affected. These results are explained qual. by considering the valence MO's of a distorted spiropentane. Quantum chemical calcns. using the 3-21 G basis set confirm this picture.

L5 ANSWER 60 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN

AN 1992:563434 CAPLUS

DN 117:163434

TI Antiestrogenic effects of (Z)-1,1-dichloro-2,3 diphenyl-2-(4-methoxyphenyl)cyclopropane on human breast cancer cells in culture

AU Jain, Pramod T.; Pento, J. Thomas; Magarian, Robert A.

CS Coll. Pharm., Univ. Oklahoma, Oklahoma City, OK, 73190, USA

SO Anticancer Research (1992), 12(3), 585-90

CODEN: ANTRD4; ISSN: 0250-7005

DT Journal LA English

GI

AB The antiproliferative activity of the title compound (I) was examined on estrogen receptor (ER)-pos. MCF-7 and ER-neg. MDA-MB-231 human breast cancer cells and A-549 human lung cancer cells using the hemocytometric trypan blue exclusion method. I inhibited the growth of MCF-7 cells in a dose-related manner over a concentration range of 10-9 to 10-5 M, but did not alter the growth of MDA-MB-231 or A-549 cells. Co-administration of estradiol (10-8 M) reversed the antiproliferative activity of I (10-7 M) on MCF-7 cells. Further, an ER-dependent mechanism of action is supported by the specific ER binding of I in MCF-7 cells observed in this study. The influence of I on the cell surface morphol. of MCF-7 and MDA-MB-231 cells was studied using SEM. Compound I at 10-6 M reduced the length and d. of microvilli (MV) on MCF-7 cells, which was reversed by co-administration of estradiol (10-8 M). This compound did not alter the cell surface morphol. of ER-neg. MDA-MB-231 cells. In conclusion, I and tamoxifen inhibited the growth of ER-pos. MCF-7 cells in an estradiol-reversible manner, and had no effect on ER-neg. MDA-MB-231 cells. The results of this study with human breast cancer cells suggest that I may be highly effective in the treatment of estrogen-dependent breast cancer and/or in the prophylactic treatment of women with a high risk of breast cancer development.

L5 ANSWER 61 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN

AN 1992:420029 CAPLUS

DN 117:20029

TI Synthesis and biological evaluation of a series of gemdichlorocyclopropanes as antitumor agents

AU Griffin, May T.; Magarian, Robert A.; Jain, Pramod; Pento, J. Thomas; Mousissian, Gorgin K.; Graves, Don C.

CS Coll. Pharm., Univ. Oklahoma, Oklahoma City, OK, 73190, USA

SO Anti-Cancer Drug Design (1992), 7(1), 49-66

CODEN: ACDDEA; ISSN: 0266-9536

Ι

DT Journal

LA English

GI

но

AB A series of Analog II (1,1-dichloro-2,3-diphenylcyclopropane) derivs. demonstrating lower intrinsic estrogenicity was synthesized. The compds. were tested for their ability to inhibit the growth-stimulating action of estradiol in the immature mouse uterus and estrogen receptor (ER) (+) MCF-7 human breast cancer cells in vitro. Like Analog II, the derivs.

were found to have no intrinsic estrogenicity (except I) and they antagonized estradiol action less completely than the lead compound Polarity improved the ER binding affinity of Analog II, but was quite small for all compds., except I, for which it was comparable to tamoxifen. Six compds. demonstrated antiproliferative activity toward MCF-7 cells, in vitro, and the mean inhibition period over 6 days ranged from 20 to 37%. Only I was reversed by estradiol.

- L5 ANSWER 62 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
- AN 1992:173590 CAPLUS
- DN 116:173590
- TI Reaction of a chiral cyclopropyl halide with alkali metals in alcohol solvents. The surface nature of the reaction
- AU Walborsky, H. M.; Ollman, J.; Hamdouchi, C.; Topolski, M.
- CS Dittmer Lab. Chem., Florida State Univ., Tallahassee, FL, 32306, USA
- SO Tetrahedron Letters (1992), 33(6), 761-4
 - CODEN: TELEAY; ISSN: 0040-4039
- DT Journal
- LA English
- OS CASREACT 116:173590
- AB An alc. solution (MeOH, Me2CHOH, Me3COH) of (S)-(+)-1-bromo-1-methyl-2,2-diphenylcyclopropane was treated with an alkali metal (Li, Na, K). The resultant hydrocarbon, (R)-(-)-1-methyl-2,2-diphenylcyclopropane, was optically active and with retained configuration. As in Grignard reagent formation, the reactions are viewed as occurring largely on the surface of metal.
- L5 ANSWER 63 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
- AN 1992:120484 CAPLUS
- DN 116:120484
- TI Antiproliferative activity of a series of novel cyclopropyl antiestrogens on MCF-7 human breast cancer cells in culture
- AU Jain, Pramod T.; Pento, J. Thomas; Magarian, Robert A.; Graves, Donald C.
- CS Coll. Pharm., Univ. Oklahoma, Oklahoma City, OK, 73190, USA
- SO Anti-Cancer Drugs (1991), 2(5), 487-93 CODEN: ANTDEV; ISSN: 0959-4973
- DT Journal
- LA English
- The potential antitumor activity of a series of novel cyclopropyl compds., which lack estrogen agonist activity, was evaluated in estrogen receptor pos. human breast cancer cells (MCF-7) in culture. The compds. were evaluated to determine their antiproliferative activity at a concentration of 1 μ M at 2, 4 and 6 days of treatment by hemocytometer using the Trypan Blue exclusion method to count viable cells. Estradiol-induced reversibility of the antiproliferative activity of these compds. was also evaluated. The activity of a series of 19 diaryl- and triaryl cyclopropyl compds. was examined Thirteen compds. inhibited the growth of MCF-7 cells while six were inactive. Five of the 13 active compds. produced antiproliferative activity which was reversed by 0.1 μ M estradiol. Thus, several of these novel cyclopropyl compds. may be useful in the treatment of hormone-dependent breast cancer and other estrogen-dependent tumors.
- L5 ANSWER 64 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
- AN 1992:40923 CAPLUS
- DN 116:40923
- TI Reaction of chiral cyclopropyl halides with samarium diiodide
- AU Walborsky, H. M.; Topolski, Marek
- CS Dittmer Lab. Chem., Florida State Univ., Tallahassee, FL, 32306-3006, USA
- SO Journal of Organic Chemistry (1992), 57(1), 370-3 CODEN: JOCEAH; ISSN: 0022-3263
- DT Journal
- LA English
- OS CASREACT 116:40923
- AB The reduction of (S)-1-bromo-1-methyl-2,2-diphenylcyclopropane (I),
 - (S)-1-bromo-1-(methoxymethyl)-2,2-diphenylcyclopropane, and
 - (R)-1-fluoro-1-iodo-2,2-diphenylcyclopropane with SmI2 was reported.
 - Evidence for the formation of a Sm(III) intermediate was presented. The reaction of I with SmI2 gave 58% (R)-1-methyl-2,2-diphenylcyclopropane (78% retention of configuration), 22% 2-methyl-1,1-diphenyl-1-propene, and

2% 2,5-dimethyl-1,1,6,6-tetraphenyl-1,5-hexadiene.

- L5 ANSWER 65 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
- AN 1991:655653 CAPLUS
- DN 115:255653
- TI General and convenient route to alkenylidenecyclopropanes: generation of alkenylidenecarbene from 1,1-dibromocyclopropanes under phase-transfer conditions
- AU Isaqawa, Kakuzo; Mizuno, Kazuhiko; Sugita, Hikaru; Otsuji, Yoshio
- CS Dep. Appl. Chem., Univ. Osaka Prefect., Sakai, 591, Japan
- SO Journal of the Chemical Society, Perkin Transactions 1: Organic and Bio-Organic Chemistry (1972-1999) (1991), (9), 2283-5 CODEN: JCPRB4; ISSN: 0300-922X
- DT Journal
- LA English
- OS CASREACT 115:255653

GI

$$R^{1}$$
 R^{2}
 R^{2}
 R^{3}
 R^{4}
 R^{5}
 R^{5}
 R^{6}
 R^{6}

- Alkenylidenecyclopropane have been prepared in a stereospecific manner by the reaction of 1,1-disubstituted 2,2-dibromocyclopropanes with NaOH under phase-transfer conditions in the presence of alkenes. Thus, treating dibromocyclopranes I (R1 = Me, Ph, 2-naphthyl; R2 = Me, Ph) with aqueous NaOH (or powdered NaOH) in the presence of Bu4NHSO4 and alkenes R3R4C:CR5R6 (R3-R6 = Me, Ph, etc.) in C6H6 gave good yields of the alkenylidenecyclopropanes
- L5 ANSWER 66 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
- AN 1991:655650 CAPLUS
- DN 115:255650
- TI Unusual addition of 1,2-alkylidenecarbenes to 1,3-dienes: 1,4-addition of rigid and flexible 1,3-dienes
- AU Sugita, Hikaru; Mizuno, Kazuhiko; Mori, Toshiki; Isagawa, Kakuzo; Otsuji, Yoshio
- CS Coll. Eng., Univ. Osaka Prefect., Sakai, 591, Japan
- SO Angewandte Chemie (1991), 103(8), 1000-2 (See also Angew. Chem., Int. Ed. Engl., 1991, 30(8), 984-6)
 CODEN: ANCEAD; ISSN: 0044-8249
- DT Journal
- LA German
- OS CASREACT 115:255650
- AB 3,3-Disubstitued alkylidene carbenes, generated from 1,1-dibromo-2,2-disubstituted cyclopropanes via double dehydrobromination under phase-transfer conditions, add to rigid and non-rigid 1,3-dienes to give 1,2- and 1,4-adducts in appreciable amts.
- L5 ANSWER 67 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
- AN 1991:631848 CAPLUS
- DN 115:231848
- TI Preparation of 1,1-dichloro-2,2,3-triarylcyclopropanes as antiestrogenic and antitumor agents
- IN Magarian, Robert A.; Pento, Joseph T.; Day, Billy W.
- PA University of Oklahoma, USA
- SO U.S., 12 pp. Cont.-in-part of U.S. 4,879,315. CODEN: USXXAM
- DT Patent
- LA English
- FAN.CNT 7

	PATENT NO.	KIND DATE		APPLICATION NO.	DATE	
PΙ	US 5015666	Α	19910514	US 1989-410938	19890922 <	

	US 4879315	Α	19891107	US 1987-98945	19870921 <
PRAI	US 1980-128040	B2	19800307		
	US 1980-166255	B2	19800707		
	US 1982-363429	B2	19820330		
	US 1987-98945	A2	19870921		
os	MARPAT 115:231848				
GI					

$$R^2$$
 X
 R^4
 R^3

The title compds. [I; R1 = H, HO, alkoxy, (un) substituted arylalkoxy; R2, R3 = H, HO, (un) substituted alkoxy, (alkyl) aryl; R4 = H; X = H, halo] or their pharmaceutically acceptable salts, were prepared Addition reaction of 4-MeOC6H4MgBr with PhCH2COC6H4(OCH2Ph)-4 gave 2,2-diarylethene PhCH:C(C6H4OMe-4)C6H4(OCH2Ph)-4 which underwent a dichlorocarbene addition reaction to give the appropriate (R/S)-(Z)-cyclopropane. This, after debenzylation by H over Pd/C, gave title compound (R/S)-(Z)-I (R1 = 4-HO, R2 = 4-MeO, R3 = R4 = H, X = Cl) (II) which in vitro in an estrogen receptor binding assay had receptor binding activity of 2.40% (estradiol = 100%). II at 30 μ g in mice gave 28% inhibition of estradiol-induced uterotrophic activity, while tamoxifen had no antagonistic activity at doses of 30, 150, and 750 μ g.

L5 ANSWER 68 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN

Ι

AN 1991:514036 CAPLUS

DN 115:114036

TI Metal catalyzed carbonylation of gem-dibromocyclopropanes

AU Grushin, Vladimir V.; Alper, Howard

CS Ottawa-Carleton Chem. Inst., Univ. Ottawa, Ottawa, ON, K1N 6N5, Can.

Tetrahedron Letters (1991), 32(28), 3349-52

CODEN: TELEAY; ISSN: 0040-4039

DT Journal

SO

GI

LA English

OS CASREACT 115:114036

Ph

Br Br T CO2H T

The first examples of the catalytic carbonylation of gemdibromocyclopropanes is described, using cobalt and nickel salts as catalysts under phase transfer conditions. Thus, 1,1-dibromo-2phenylcyclopropane (I) in PhMe was added to a mixture of 5N KOH, CoCl2, Ni(CN)2.4H2O, KCN, and PEG-400 in PhMe that had been pretreated with CO-H2 and the mixture heated under CO-H2 to give 72% a 1:1 mixture of the cis- and trans-phenylcyclopropanecarboxylic acids II.

L5 ANSWER 69 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN

AN 1991:255584 CAPLUS

DN 114:255584

- TI Mediated electrochemical reduction of 1,1-dichlorocyclopropanes
- AU Yanilkin, V. V.; Maksimyuk, N. I.; Gritsenko, E. I.; Kargin, Yu. M.
- CS Inst. Org. Fiz. Khim. im. Arbuzova, Kazan, USSR
- SO Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya (1991), (1), 261-2
 - CODEN: IASKA6; ISSN: 0002-3353
- DT Journal
- LA Russian
- AB The unexpected possibility was observed of multiple acceleration of an electrochem. reaction with the participation of organic electron carriers with the substrate owing to the assistance of metal ions. The electrochem. monodechlorination of substituted 1,1-dichlorocyclopropanes (as substrates) showed that the effective rate constant (keff,M-1c-1) of electron transfer with the anion-radical of anthracene on the substrate increases in the presence of Ni(II) and Co(II) ions from 2- to 16-fold.
- L5 ANSWER 70 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
- AN 1991:163568 CAPLUS
- DN 114:163568
- TI Formation of a chiral 1-fluoro-2,2-diphenylcyclopropyl radical in the Barton decarboxylation reaction
- AU Gawronska, K.; Gawronski, J.; Walborsky, H. M.
- CS Dittmer Lab. Chem., Florida State Univ., Tallahassee, FL, 32306-3006, USA
- SO Journal of Organic Chemistry (1991), 56(6), 2193-7 CODEN: JOCEAH; ISSN: 0022-3263
- DT Journal
- LA English
- OS CASREACT 114:163568
- GI For diagram(s), see printed CA Issue.
- AB The chiral 1-fluoro-2,2-diphenylcyclopropyl radical (I), generated in the Barton decarboxylation reaction, was used as a probe to evaluate a variety of halogen and hydrogen atom donating reagents as radical traps. Thus, reaction of (+)-(R)-1-fluoro-2,2-diphenylcyclopropanecarbonyl chloride with BrCCl3 in the presence of sodium 2-mercaptopyridine N-oxide and 4-(dimethylamino)pyridine gave 78% (+)-(S)-1-bromo-1-fluoro-2,2-diphenylcyclopropane.
- L5 ANSWER 71 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
- AN 1991:121235 CAPLUS
- DN 114:121235
- TI Mass spectra of 1-aryl-2,2-dibromocyclopropanes
- AU Lin, Shaw Tao; Lin, Mei Ling; Lin, Wen Chung
- CS Dep. Appl. Chem., Providence Univ., Taichung, 43309, Taiwan
- SO Organic Mass Spectrometry (1990), 25(12), 667-70 CODEN: ORMSBG; ISSN: 0030-493X
- DT Journal
- LA English
- AB The electron impact (EI) mass spectra of sixteen 1-aryl-2,2-dibromocyclopropanes give an ion at m/x 115, the structure of which is proposed to be the indenium ion based on a collision-activated decomposition experiment
- L5 ANSWER 72 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
- AN 1991:101306 CAPLUS
- DN 114:101306
- TI Synthesis and biological evaluation of a series of 1,1-dichloro-2,2,3-triarylcyclopropanes as pure antiestrogens
- AU Day, Billy W.; Magarian, Robert A.; Jain, Pramod T.; Pento, J. Thomas; Mousissian, Gorgin K.; Meyer, Karen L.
- CS Coll. Pharm., Univ. Oklahoma, Oklahoma City, OK, 73190, USA
- SO Journal of Medicinal Chemistry (1991), 34(2), 842-51 CODEN: JMCMAR; ISSN: 0022-2623
- DT Journal
- LA English
- OS CASREACT 114:101306
- GI

AB A series of 1,1-dichloro-2,2,3-triarylcyclopropanes, including I (R = MeO, R1 = R2 = H; R = PhCH2O, R1 = MeO, R2 = H), was synthesized and evaluated as pure antiestrogens. Addition of 4-methoxy- or 4-(benzyloxy)phenyl Grignard reagents to p-methoxy, p-benzyloxy, or unsubstituted deoxybenzoins, followed by dehydration of the resulting carbinols produced a mixture of E and Z olefins, which reacted with dichlorocarbene to give O-protected I. The E and Z isomers were separated by fractional crystallization and the central or geminal Ph ring was deprotected to provide phenolic I. Alkylation with (N,N-dimethylamino)ethyl chloride yielded basic cyclopropanes. Two chlorodiarylindenes II (R = Me, PhCH2) were isolated as thermolysis products of I, and one was converted to II (R = H) by hydrogenolysis. All I and II were competitive inhibitors of [3H]-estradiol binding in the immature rat uterine cytosol receptor assay, with relative binding affinities of 0.1-3.6% of estradiol. None of the new compds. were estrogenic in the 3-day immature mouse uterotrophic assay at doses up to 750 μ g. In the 3-day immature mouse antiuterotrophic assay. five I (R = MeO, Me2NCH2CH2O, R1 = R2 = H; R = PhCH2O, R1 = R2 = RMeO; R = PhCH2O, R1 = MeO, R2 = H; R = Me2NCH2CH2O, R1 = MeO, R2 = H) produced significant decreases in uterine weight at doses up to 750 μg. One compound, I (R = Me2NCH2CH2O, R1 = MeO, R2 = H), elicited a dose-dependent decrease in vivo comparable to Mer 25. These same five compds., as well as the lead compound 1,1-dichloro-2,3-cisdiphenylcyclopropane were active in vitro against the estrogen-dependent MCF-7 human breast tumor cell line in a dose-dependent fashion.

L5 ANSWER 73 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN

AN 1990:590594 CAPLUS

DN 113:190594

TI Radical intermediates during reduction of halocyclopropanes by lithium aluminum hydride

AU Hatem, J.; Waegell, B.

CS Lab. Stereochim., Fac. Sci. Saint-Jerome, Marseille, 13397, Fr.

SO Tetrahedron (1990), 46(8), 2789-806 CODEN: TETRAB; ISSN: 0040-4020

DT Journal

LA French

OS CASREACT 113:190594

AB Evidence for a radical intermediate in the lithium aluminum hydride reduction of halocyclopropanes is obtained from the comparison of the stereochem. outcome of this reaction with tributyltin hydride, dimsylsodium and sodium methoxy ethoxy aluminum hydride.

- L5 ANSWER 74 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
- AN 1990:515142 CAPLUS
- DN 113:115142
- TI Selectivity in reactions of 3,3-disubstituted cyclopropenes with nitrile
- AU Bolesov, I. G.; Ignatchenko, A. V.; Bovin, N. V.; Prudchenko, I. A.; Surmina, L. S.; Plemenkov, V. V.; Petrovskii, P. V.; Romanov, I. V.; Mel'nik, I. I.

CS Mosk. Gos. Univ., Moscow, USSR

SO Zhurnal Organicheskoi Khimii (1990), 26(1), 102-19

CODEN: ZORKAE; ISSN: 0514-7492

DT Journal LA Russian

OS CASREACT 113:115142

GΙ

AB Cycloaddn. of cyclopropenes I (R1 = Me, R2 = Me, Ph, 4-BrC6H4, CH:CH2, CH2:CMe, Me2C:CH, CN; R1 = R2 = Ph) with R3CN+O- (R3 = 4-BrC6H4, 4-ClC6H4, 4-O2NC6H4, MeO2C, CN), generated in situ from the appropriate imidoyl chlorides, gave 7-98% stereoisomeric oxaazabicyclohexenones II and III. Cyclopropenes I were prepared by addition of CHBr3 to appropriate dienes and alkenes.

- L5 ANSWER 75 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
- AN 1990:459254 CAPLUS
- DN 113:59254
- TI Mechanism of grignard reagent formation. The surface nature of the reaction [Erratum to document cited in CA110(15):135283e]
- AU Walborsky, H. M.; Rachon, Janusz
- CS Dittmer Lab. Chem., Florida State Univ., Tallahassee, FL, 32306, USA
- SO Journal of the American Chemical Society (1990), 112(10), 4090 CODEN: JACSAT; ISSN: 0002-7863
- DT Journal
- LA English
- AB An error in the label for structure 4 has been corrected. The error was not reflected in the abstract or the index entries.
- L5 ANSWER 76 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
- AN 1990:216412 CAPLUS
- DN 112:216412
- TI Preparation of diphenylcyclopropanes as antiestrogenic, antitumor and female fertility agents
- IN Magarian, Robert A.; Pento, Joseph T.
- PA University of Oklahoma, USA
- SO U.S., 17 pp. Cont.-in-part of U.S. Ser. No. 363,429, abandoned. CODEN: USXXAM
- DT Patent
- LA English
- FAN. CNT 7

L MIA . /	CTA T	•						
	PAT	TENT NO.	KIND	DATE	ΑP	PLICATION NO.	DATE	
ΡI	US	4879315	Α	19891107	US	1987-98945	19870921	<
	US	5015666	Α	19910514	US	1989-410938	19890922	<
	US	5098903	Α	19920324	US	1989-432564	19891106	<
	US	5397802	Α	19950314	US	1993-20922	19930222	<
	US	5324736	Α	19940628	US	1993-107426	19930816	<
	US	5422367	Α	19950606	US	1994-201737	19940225	<
	US	5663207	Α	19970902	US	1995-376961	19950120	<
	US	5658927	Α	19970819	US	1995-480212	19950607	<
	US	5658914	Α	19970819	US	1995-480215	19950607	<
	US	5658951	Α	19970819	US	1995-487717	19950607	<
PRAI	US	1980-128040	A2	19800307				
	US	1980-166255	A2	19800707				
	US	1982-363429	A2	19820330				
	US	1987-98945	A2	19870921				

US	1989-432564	A2	19891106
US	1991-812246	B2	19911219
US	1993-20922	A1	19930222
US	1993-107426	Ą3	19930816
US	1995-376961	A2	19950120
MA	RPAT 112:216412		

R1 R4

AB The title compds. [I; R1 = H, alkyl, (un) substituted monocyclic group; R2 = H, OH, OAc, alkoxy, etc.; R3 = H, OH, OAc, alkoxy; R4 = H, alkyl; X = H, halo] were prepared Thus, cis-stilbene was refluxed 2.5 h with PhHgCCl2Br in benzene to give 86% cis-I (R1-R4 = H; X = Cl) which suppressed growth of 7,12-dimethylbenz[a]anthracene-induced tumors in rats receiving 0.6 mg s.c. 3 times weekly, to ≤5 cm3 (control = 40 cm3) after 6 wk.

- L5 ANSWER 77 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
- AN 1990:215972 CAPLUS
- DN 112:215972

os GI

- TI Mechanism of Grignard reagent formation. Further evidence for the surface nature of the reaction
- AU Rachon, Janusz; Walborsky, H. M.
- CS Dep. Chem., Florida State Univ., Tallahassee, FL, 32306, USA
- SO Tetrahedron Letters (1989), 30(52), 7345-8
 - CODEN: TELEAY; ISSN: 0040-4039
- DT Journal
- LA English
- OS CASREACT 112:215972
- AB The use of Rieke magnesium permits one to obtain reaction with (S)-(+)-1-bromo-1-methyl-2,2-diphenylcyclopropane at -65° to yield a chiral Grignard reagent that is 33-43% optically pure.
- L5 ANSWER 78 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
- AN 1990:98044 CAPLUS
- DN 112:98044
- TI Behavior of dibromocarbene towards substituted aryl aliphatic olefins
- AU Moussa, G. E. M.; Shaban, M. E.; Girgis, D. B.
- CS Fac. Sci., Ain Shams Univ., Cairo, Egypt
- SO Egyptian Journal of Chemistry (1988), Volume Date 1987, 30(1), 77-83
 - CODEN: EGJCA3; ISSN: 0367-0422
- DT Journal
- LA English
- OS CASREACT 112:98044
- AB Steric factors play a significant role in controlling the rate of dibromocarbene addition to tri- and tetraaryl substituted ethylenes. The transition state was discussed.
- L5 ANSWER 79 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
- AN 1990:20932 CAPLUS
- DN 112:20932
- TI A synthetic route to bicyclic pyrazolenines via 3-chloropyrazolines and the ring opening of pyrazolenines to diazoalkenes
- AU Nakano, Yoshihiko; Hamaguchi, Masashi; Nagai, Toshikazu
- CS Coll. Gen. Educ., Osaka Univ., Osaka, 560, Japan
- SO Journal of Organic Chemistry (1989), 54(25), 5912-19 CODEN: JOCEAH; ISSN: 0022-3263
- DT Journal
- LA English
- OS CASREACT 112:20932

Treatment of 5,5-disubsituted 3-chloro-1-pyrazolines, derived from the reaction between disubstituted diazomethanes and di-Me chlorofumarate, with triethylamine gives the corresponding 3,3-disubstituted 3H-pyrazoles in good yield. This method was applied to the synthesis of bicyclic pyrazolenines. The system fused to a 5-membered imide ring did not afford 3H-pyrazoles but diazoalkenes, e.g. I, formed by thermal ring opening of the 3H-pyrazoles. In contrast, in a 6-membered ring fused system, the 3H-pyrazoles, e.g. II, were isolated. The isolation of diazoalkenes from the 5-membered ring fused system is explained by destabilization of the 3H-pyrazoles due to strain arising from fusion of 2 five-membered rings.

L5 ANSWER 80 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN

AN 1989:231388 CAPLUS

DN 110:231388

TI [2 + 4] Photocyclization between quinones and allenes via photoinduced electron transfer

AU Maruyama, Kazuhiro; Imahori, Hiroshi

Fac. Sci., Kyoto Univ., Kyoto, 606, Japan

SO Journal of Organic Chemistry (1989), 54(11), 2692-702

CODEN: JOCEAH; ISSN: 0022-3263

DT Journal

LA English

OS CASREACT 110:231388

GΙ

CS

AB Photochem. reactions of halo-1,4-naphthoquinones with 1,1-diphenylallenes afforded spiro pyran adducts derived from regioselective [2 + 4] cycloaddn. between the CO group of the quinone and the allene. E.g., Ph2C:C:CH2 and 2,3-dichloro-1,4-naphthoquinone (I) gave spiro(benzopyrannaphthalenone) II (R = H). The structure of II (R = Me) was determined by x-ray crystallog. In the photoreactions of I with p-R1C6H4CH:C:CH2 (R1 = H, Me), [2 + 2] cycloadducts III were obtained in addition to spiro pyran derivs. On the basis of the free energy changes together with substituent effects, solvent effects, and CIDNP data, an electron-transfer mechanism is plausible. Radical ion pair formation of

an excited triplet quinone and an allene is followed by conversion to a biradical. Subsequent bond formation between the ketyl radical in the quinone moiety and the ortho position of a Ph substituent on the allene skeleton leads to the spiro pyran adduct after a subsequent 1,5-H shift.

- L5 ANSWER 81 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
- AN 1989:192011 CAPLUS
- DN 110:192011
- TI Applications of phase-transfer catalysis. Part 41. Cocatalytic effects of pinacol in phase-transfer catalysis
- AU Dehmlow, Eckehard V.; Raths, Hans Christian; Soufi, Johanna
- CS Fak. Chem., Univ. Bielefeld, Bielefeld, D-4800/1, Fed. Rep. Ger.
- SO Journal of Chemical Research, Synopses (1988), (10), 334-5
- CODEN: JRPSDC; ISSN: 0308-2342
- DT Journal
- LA English
- OS CASREACT 110:192011
- AB Yields of dihalocyclopropanes made by phase-transfer catalysis (PTC) from bromoform or chloroform are higher if a small concentration of pinacol is present as cocatalyst. It is shown that pinacol accelerates PTC deprotonation of substrates up to pKa 27; beyond that a rate decrease is found.
- L5 ANSWER 82 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
- AN 1989:154210 CAPLUS
- DN 110:154210
- TI Addition of diphenyldiazomethane to unsubstituted and chloro-substituted 1,4-benzoquinones. Effects of chloro substituents on the addition modes
- AU Oshima, Takumi; Nagai, Toshikazu
- CS Coll. Gen. Educ., Osaka Univ., Toyonaka, 560, Japan
- SO Bulletin of the Chemical Society of Japan (1988), 61(7), 2507-12 CODEN: BCSJA8; ISSN: 0009-2673
- DT Journal
- LA English
- OS CASREACT 110:154210

Ι

III

GΙ

L5

AB Unsubstituted 1,4-benzoquinone reacted with dipheyldiazomethane (DDM) at the C:C double bonds to give dihydroxy-3H-indazole (I) and its benzhydryl ether together with benzodipyrazole derivative (II). Similarly, reactions of 2-chloro- and 2,3-dichloro-1,4-benzoquinones with DDM yielded the corresponding dihydroxy-3H-indazoles and their benzhydryl ethers along with 5-13% benzophenone. Reaction of 2,6-dichloro-1,4-benzoquinone with DDM gave bicyclic III and tricyclic diones (IV) together with benzophenone di-Me acetal in the presence of added methanol. In the same conditions, 2,3,5-trichloro-1,4-benzoquinone provided its bicyclic dione and benzophenone di-Me acetal. The C = O addition increased with increasing chlorine substituents.

IV

ANSWER 83 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN

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AN 1989:135283 CAPLUS
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- DN 110:135283
- TI Mechanism of Grignard reagent formation. The surface nature of the reaction
- AU Walborsky, H. M.; Rachon, Janusz
- CS Dittmer Lab. Chem., Florida State Univ., Tallahassee, FL, 32306, USA
- SO Journal of the American Chemical Society (1989), 111(5), 1896-7 CODEN: JACSAT; ISSN: 0002-7863
- DT Journal
- LA English
- AB Further evidence for the surface nature of Grignard reagent formation is provided in the reaction of chiral 1-bromo-1-methyl-2,2-diphenylcyclopropane, 4-methylcyclohexylidene-1-bromoethane and Me 2-bromodibenzobicyclo[2.2.2]octane-2-carboxylate with magnesium in methanol solvent.
- L5 ANSWER 84 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
- AN 1989:114749 CAPLUS
- DN 110:114749
- TI Stability and stereochemistry in the decomposition of pentasubstituted 1-pyrazolines controlled by interactions between bulky vicinal substituents
- AU Nakano, Yoshihiko; Hamaguchi, Masashi; Nagai, Toshikazu
- CS Coll. Gen. Educ., Osaka Univ., Osaka, 560, Japan
- SO Journal of Organic Chemistry (1989), 54(5), 1135-44
- CODEN: JOCEAH; ISSN: 0022-3263
- DT Journal
- LA English

GI

OS CASREACT 110:114749

- 1,2-Diacyl-1-chloroethylenes [e.g., (Z) and (E)-MeO2CCCl:CHCO2Me) reacted AB with disubstituted diazomethanes (e.g., Me2C:N2, MeCPh:N2, Ph2C:N2) to give pyrazolines and cyclopropanes (e.g., I and II, resp.). The thermal decomposition of the isolated pyrazolines was carried out. The thermal stability of the pyrazolines increased with the variation of the substituents at C5 in the order biphenylylene < Ph, Ph < Ph, Me < Me, Me, while pyrazolines bearing bulky vicinal substituents at C3, C4, and C5 in the cis configuration were substantially more stable than other isomers. This abnormal stability is explained by the reasonable expectation that bulky C4 substituents partly inhibit conformations of the conjugated substituents at C3 or C5 favorable for the decomposition, which increases the activation energy. Although most of the thermolyses of the pyrazolines to cyclopropanes gave products with the same configuration as the starting materials, some pyrazolines bearing bulky vicinal cis groups gave mixts. of stereoisomeric cyclopropanes. The thermolysis mechanism is discussed.
- L5 ANSWER 85 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
- AN 1989:74532 CAPLUS
- DN 110:74532
- TI Studies on phase transfer catalysis. V. Kinetic study of the cycloaddition of dibromocarbene with substituted styrenes and α -arylstyrenes by carbon-14 labeling method
- AU Lin, Shouyuan; Wu, Yuling; Wang, Zhizhong; Sheng, Huaiyu
- CS Shanghai Inst. Org. Chem., Acad. Sin., Shanghai, Peop. Rep. China
- SO Huaxue Xuebao (1988), 46(5), 419-26 CODEN: HHHPA4; ISSN: 0567-7351
- DT Journal
- LA Chinese
- OS CASREACT 110:74532

The relative rate consts. krel of the PTC reaction of p-substituted styrenes I (R = H, Me, Cl, MeO, NO2) with dibromocarbene were measured by radiocounting method and the krel values were analyzed by linear correlation method. The $\rho+$ value of the PTC reaction of $\alpha\text{-arylstyrenes}$ II (R1 = 3-Me, 4-Me, H, 3-Cl, 4-MeO, 3-CF3) with dibromocarbene system was smaller than the one obtained from substituted styrene reaction. It was suggested that the aryl group of $\alpha\text{-arylstyrene}$ might disperse the pos. charge from α carbon atom. A variety of the crown compds. were used as PTC catalysts for the reaction of 1,1-diphenylethylene and dibromocarbene and it was found that N,N'-disubstituted azacrown possessed the highest catalytic activity for this reaction. Six 1-14C-1, 1-dibromo-2-aryl-2-phenyl-cyclopropanes were prepared and identified by comparison with the unlabeled authentic samples III which were characterized by elemental anal., NMR, MS, and TLC anal.

L5 ANSWER 86 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN

AN 1988:510017 CAPLUS

DN 109:110017

TI Preparation of (phenylthio) cyclopropane derivatives as pyrethroid-type insecticides

IN Suzuki, Hitomi

PA Daikin Industries, Ltd., Japan

SO Jpn. Kokai Tokkyo Koho, 4 pp.

CODEN: JKXXAF

DT Patent

LA Japanese

FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE	
PI	JP 63101358	A2	19880506	JP 1986-248112	19861017 <	
PRAI	JP 1986-248112		19861017			
os	CASREACT 109:110017;	MARPAT	109:110017			
GI						

AB Title derivs. I (R1 - R4 = H, alkyl, alkoxy, aryl; R1R2 = 2-C6H4CH2CH2CH2), useful as pyrethroid-type insecticides (no data), are prepared from PhSCHFCl (II) and R1R2C:CR3R4. A mixture of Me2C:CMe2, PhCH2N+Et3 Cl-, and NaOH in CH2Cl2-H2O was treated with II at room temperature for 4-5 h to give 84% I (R1 - R4 = Me).

L5 ANSWER 87 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN

AN 1988:405925 CAPLUS

DN 109:5925

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TI Arylcyclopropane photochemistry. Effects of electron-donating and electron-withdrawing aromatic substituents on the photochemical rearrangements of 1,1-diarylcyclopropanes
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AU Hixson, Stephen S.; Franke, Lothar A.

CS Chem. Dep., Univ. Massachusetts, Amherst, MA, 01003, USA

Journal of Organic Chemistry (1988), 53(12), 2706-11

CODEN: JOCEAH; ISSN: 0022-3263

DT Journal LA English

OS CASREACT 109:5925

GI

SO

AB Irradiation of 1,1-diarylcyclopropanes I (R, R1 = CF3, CN, H, OMe, Me) afforded 1,1-diarylpropenes and 1-arylindans. The rate consts. of these (singlet state) reactions were determined from the reactant fluorescence lifetimes and product quantum yields. The rate-determining step in the rearrangements is charge-transfer-enhanced cyclopropane ring opening.

L5 ANSWER 88 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN

AN 1987:459101 CAPLUS

Ι

DN 107:59101

TI Versatile synthesis of dialkyl cyclopropylphosphonates via reductive phosphonation

AU Hirao, Toshikazu; Hagihara, Masahiko; Agawa, Toshio

CS Fac. Eng., Osaka Univ., Suita, 565, Japan

SO Bulletin of the Chemical Society of Japan (1985), 58(11), 3104-7

CODEN: BCSJA8; ISSN: 0009-2673

DT Journal

LA English

OS CASREACT 107:59101

GI

AB Reductive phosphonation of gem-dibromocyclopropane I [R1 = n-C6H13, H, Ph, SiMe3, CN; R2 = H, Me; R3 = H; R2R3 = (CH2)4, (CH2)6] with P(OR4)3 (R4 = Et, Me2CH) in the presence of Et3N and water gave cis- and trans-cyclopropylphosphonates II, along with the corresponding monobromocyclopropanes III.

L5 ANSWER 89 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN

AN 1987:422806 CAPLUS

DN 107:22806

TI Further evidence of SET (single electron transfer) mechanism during the lithium aluminum hydride reduction of optically active 1-bromo-1-methyl-2,2-diphenylcyclopropane

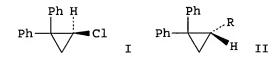
- AU Hatem, J.; Meslem, J. M.; Waegell, B.
- CS Lab. Stereochim., Univ. d'Aix-Marseille, Marseille, 13397, Fr.
- SO Tetrahedron Letters (1986), 27(32), 3723-4 CODEN: TELEAY; ISSN: 0040-4039
- DT Journal
- LA English
- AB Bu3SnH and LiAlH4 reduced the (-)-(R)-isomer of the title cyclopropane with racemization. On the other hand, similar reduction using NaAlH(OMe)(OEt) gave retention of configuration. Thus, reduction of the cyclopropyl halide by LiAlH4 proceeded via a radical intermediate, and most likely involved a SET mechanism.
- L5 ANSWER 90 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
- AN 1986:224846 CAPLUS
- DN 104:224846
- TI Oxymetalation. 20. Conversion of cyclopropanes into 1,2-dioxolanes via tert-butyl peroxymercuration, bromodemercuration, and silver salt induced cyclization
- AU Bloodworth, A. J.; Chan, Kam Hung; Cooksey, Christopher J.
- CS Christopher Ingold Lab., Univ. Coll. London, London, WC1H OAJ, UK
- SO Journal of Organic Chemistry (1986), 51(11), 2110-15 CODEN: JOCEAH; ISSN: 0022-3263
- DT Journal
- LA English
- OS CASREACT 104:224846
- Et

GΙ

- The tert-Bu peroxymercurations of cyclopropane and ethyl-, phenyl-, 1,1-dimethyl-, 1-methyl-1-phenyl-, and 1,1-diphenylcyclopropane were carried out by using mercury(II) acetate, a 1-fold excess of tert-Bu hydroperoxide, and 20 mol % of perchloric acid. After anion exchange with aqueous KBr, the derived γ -bromomercuroalkyl tert-Bu peroxides were isolated (10-51%) by silica chromatog. These were converted into the corresponding γ -bromoalkyl tert-Bu peroxides (84-100%) by reaction with Br and NaBr in MeOH. The bromides were converted into the corresponding 1,2-dioxolanes, e.g. I (>80%), by treatment with silver trifluoroacetate. However, the reaction of 3-bromo-1,1-diphenylpropyl tert-Bu peroxide with silver trifluoroacetate afforded a phenoxy acetal derived from β -tert-butoxyethyl Ph ketone, which was identified by conversion into phenol plus the corresponding (2,4-dinitrophenyl)hydrazone upon treatment with acidic (2,4-dinitrophenyl)hydrazine.
- L5 ANSWER 91 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
- AN 1986:220744 CAPLUS
- DN 104:220744
- TI Quantitative structure-activity relationships of insecticidal diphenyldichlorocyclopropanes
- AU Nishimura, Keiichiro; Hirayama, Keiko; Kobayashi, Takamitsu; Fujita, Toshio; Holan, George
- CS Dep. Agric. Chem., Kyoto Univ., Kyoto, 606, Japan
- SO Pesticide Biochemistry and Physiology (1986), 25(2), 153-62 CODEN: PCBPBS; ISSN: 0048-3575
- DT Journal
- LA English
- AB Neurophysiol. activity of a series of aromatic-substituted 1,1-diphenyl-2,2-dichlorocyclopropanes (DCC analogs) in the induction of repetitive discharges in excised central nerve cords of the American cockroach was determined by an extracellular recording technique. Quant. anal. using physicochem. parameters showed that variations in the activity were parabolically correlated with the van der Waals volume of aromatic substituents. Insecticidal activity of these compds. in the American cockroach under conditions where oxidative metabolic activity was

inhibited by piperonyl butoxide was also determined. This was related to the repetitive nerve discharge activity, when transport factors were separated by using a hydrophobicity parameter. The analyses showed that the aromatic substituent effects on the neurophysiol. activity as well as the relationship between insecticidal and neurophysiol. activities are very close to those observed previously for DDT analogs including DDT, DDD, and prolan derivs.

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L5
     ANSWER 92 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
     1986:109057 CAPLUS
ΑN
DN
     104:109057
TI
     Carbenoids. Metal assisted ionization
     Walborsky, H. M.; Duraisamy, M.
AU
     Dep. Chem., Florida State Univ., Tallahassee, FL, 32306, USA
CS
     Tetrahedron Letters (1985), 26(23), 2743-6
SO
     CODEN: TELEAY; ISSN: 0040-4039
DT
     Journal
LA
     English
os
     CASREACT 104:109057
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AB Treatment of diphenylcyclopropane I with BuLi yielded cyclopropanes II (R = H, Bu, CPh2C.tplbond.CH), with overall inverted configuration. A metal-assisted ionization mechanism was proposed.

L5 ANSWER 93 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN

AN 1986:59720 CAPLUS

DN 104:59720

TI Conformations of cyclopropane derivatives. Part II. The structure and absolute configuration of (R)-(+)-1-fluoro-2,2-

AU Ries, Wolfgang H.; Bernal, Ivan
CS Chem. Dep., Univ. Houston, Houston, TX, 77004, USA
SO Journal of Molecular Structure (1985), 131(3-4), 371-81
CODEN: JMOSB4; ISSN: 0022-2860

diphenylcyclopropanecarboxylic acid

DT Journal

GI

LA English The title compound is orthorhombic, space group P212121, with a 6.172(9), b AB 7.890(2), and c 27.091(7) Å; d.(calculated) = 1.290 for Z = 4. Final R = 0.0448 (Rw = 0.0329). Atomic coordinates are given. The plane of the carboxylic group is nearly orthogonal to the plane of the cyclopropane ring (dihedral angle 99.05°) while the dihedral angles between the 2 Ph rings and the cyclopropane ring are 117.77 and 63.18° resp. The carboxylic group is not in the bisecting conformation (with respect to the angle C4-C2-C3) as shown by the values of the torsional angles O2-C1-C2-C3 (-19.68°) and O2-C1-C2-C4 (50.35°). This is a natural consequence of the steric hindrance between the cis-Ph ring and the -COOH substituent adjacent to it. One of the bonds within the cyclopropane ring is longer than the other two (1.563(9), 1.496(9),1.494(8) $ilde{\mathtt{A}}$), the longer one being associated with the disubstituted carbons. The 2 C-O bonds are 1.290(9) and 1.195(7) Å, which are within the normally expected values. The rest of the bond lengths and angles are also normal. The mols. are H bonded into infinite chains running along the length of the α (shortest) axis of the lattice.

L5 ANSWER 94 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN AN 1985:549410 CAPLUS

DN 103:149410

TI Electroorganic reactions on organic electrodes. VIII. Comparative study of monomeric and polymeric redox mediators in indirect electrochemical reduction

AU Takiguchi, Tsuyoshi; Nonaka, Tsutomu

CS Dep. Electron. Chem., Tokyo Inst. Technol., Yokohama, 227, Japan

Nippon Kagaku Kaishi (1985), (6), 1147-53

CODEN: NKAKB8; ISSN: 0369-4577

DT Journal

so

LA Japanese

Monomeric and polymeric 1-alkylpyridinium compds. as redox mediators in AB the indirect electrochem. reduction of dihalo compds. were studied comparatively in aprotic solvents. A 4-ethoxycarbonyl-1-methylpyridinium cation (I) was found to give 2 reversible cyclic voltammetric waves which may demonstrate the formation of corresponding neutral radical of I in MeCN and the anion of I at a more neg. potential. It was confirmed by both cyclic voltammetry and preparative electrolysis that meso-1,2-dibromo-1,2-diphenylethane (II) and 1,1-dibromo-2,2diphenylcyclopropane (III) could be reduced indirectly with electrogenerated the radical of I and the anion of I, resp. A Pt electrode which was chemical modified with 4-oxycarbonyl-1-methylpyridinium groups did not give any clear redox waves. At the next stage, a polymeric mediator having a mol. structure equivalent to monomeric I was examined in a similar way. Poly(4-vinyloxy-1-methylpyridinium cation) (IV) seemed to undergo reductive decomposition in DMF, while a IV with an I- counter ion coated Pt electrodemediated the reduction of II at the 1st wave potential in The current at the 2nd wave was so small that the coated-electrode could not be used for the preparative electrolysis of III. Indirect electrochem. reactions were greatly affected by the status of mediators used.

L5 ANSWER 95 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN

AN 1985:220237 CAPLUS

DN 102:220237

TI Inter- versus intramolecular Friedel-Crafts reaction of phenyl-substituted dichlorocyclopropanes

AU Anke, Lutz; Weyerstahl, Peter

CS Inst. Org. Chem., Tech. Univ. Berlin, Berlin, D-1000/12, Fed. Rep. Ger.

Chemische Berichte (1985), 118(2), 613-19

CODEN: CHBEAM; ISSN: 0009-2940

DT Journal

LA German

SO

GΙ

OS CASREACT 102:220237

Ph R C1 - C1 $R1 \quad R^2 \qquad I$

AB Friedel-Crafts reactions of Ph substituted dichlorocyclopropanes [I; R = H, Me, Ph; R1 = Me, H; R2 = Me, Ph, H; (R1R2) = (CH2)5, R = Me, Ph] yield indenes by the known intermol. reaction with benzene and 2-chloroindenes by an intramol. pathway even in the presence of benzene. 2-Chloroindenes are also formed in CS2 without benzene. The results are explained by steric factors of the chloroallyl cation reactive intermediates.

L5 ANSWER 96 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN

AN 1985:5726 CAPLUS

DN 102:5726

TI Carbon tetrachloride-dimethyl sulfone-potassium hydroxide-tert-butyl alcohol: a convenient new reagent for gem-dichloromethylenation of alkenes

AU Poon, Chi Duen; Yuen, Po Wai; Man, Tim On; Li, Chun Sing; Chan, Tze Lock

CS Chem. Dep., Chin. Univ. Hong Kong, Shatin, Hong Kong

SO Journal of the Chemical Society, Perkin Transactions 1: Organic and Bio-Organic Chemistry (1972-1999) (1984), (7), 1561-3 CODEN: JCPRB4; ISSN: 0300-922X

DT Journal LA English

AB Treatment of CCl4 with Me2SO2-KOH-Me3COH gave :CCl2 which added stereospecifically to aliphatic, cyclic, and aromatic alkenes to give gem-dichlorocyclopropanes in 45-93% yield, with retention of configuration about the C-C double bond. E.g., reaction of cis-PrCH:CHMe with CCl4-Me2SO2-KOH-Me3COH for 1.5 h gave 51% cis-1,1-dichloro-2-methyl-3-propylcyclopropane. The relative reactivities of alkenes towards the CCl4-derived :CCl2 parallel the nucleophilicities of the alkenes and indicate that free :CCl2 is probably involved.

L5 ANSWER 97 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN

AN 1984:529920 CAPLUS

DN 101:129920

TI Carbanion photochemistry. 11. 1,3-Diphenylisoindenylidene

AU Tolbert, Laren M.; Siddiqui, Shahabuddin

CS Dep. Chem., Univ. Kentucky, Lexington, KY, 40506, USA

SO Journal of the American Chemical Society (1984), 106(19),

5538-43

CODEN: JACSAT; ISSN: 0002-7863

DT Journal

LA English

OS CASREACT 101:129920

GI

AB Irradiation of 2-chloro- or 2-bromo-1,3-diphenylindenyl anion causes dehalogenation to yield a hypovalent intermediate best described as 1,3-diphenylisoindenylidene (I) or -1,2-dehydroindene (II). This intermediate undergoes facile C-H insertion, addition to electron-rich olefins, and halide interchange.

L5 ANSWER 98 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN

AN 1984:51691 CAPLUS

DN 100:51691

TI Silanes in organic synthesis. 21. Configurational stability of the 2,2-diphenyl-1-(trimethylsilyl)cyclopropyl carbanion and free radical. Absolute stereochemical assignments to select silylcyclopropanes

AU Paquette, Leo A.; Uchida, Takane; Gallucci, Judith C.

CS Evans Chem. Lab., Ohio State Univ., Columbus, OH, 43210, USA

SO Journal of the American Chemical Society (1984), 106(2), 335-40

CODEN: JACSAT; ISSN: 0002-7863

DT Journal

LA English

OS CASREACT 100:51691

GI

AB 2,2-Diphenylcyclopropanecarboxylic acid was silylated at the 1-position and this product was resolved with 1-cinchonidine. The resulting

optically active acid [(-)-I] was transformed into (-)-2,2-diphenyl-1-methyl-1-(trimethylsilyl)cyclopropane, whose absolute configuration was shown to be R by metalation and silylation of (-)-(R)-II. The latter reaction proceeds with retention of configuration. In this way, the levorotatory form of (-)-I was established to be R. Whereas the Hunsdiecker degradation of (-)-(R)-I produced only racemic bromide, application of the Haller-Bauer process to (+)-(R)-III led to (-)-(R)-IV. This carbanion-mediated reaction proceeded with complete retention of stereochem. The failure of the α -silyl cyclopropyl free radical to maintain configuration and the nonracemizability of its carbanion counterpart are discussed in the light of Si's capacity for stabilizing neighboring reactive centers.

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L5 ANSWER 99 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
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AN 1984:51201 CAPLUS

DN 100:51201

TI Study of thermal transformations of gem-dihalodiphenylcyclopropanes

AU Kostikov, R. R.; Varakin, G. S.; Ogloblin, K. A.

CS Leningr. Univ., Leningrad, USSR

Zhurnal Organicheskoi Khimii (1983), 19(8), 1625-32

CODEN: ZORKAE; ISSN: 0514-7492

DT Journal

LA Russian

OS CASREACT 100:51201

GI

SO

$$\mathbb{R}^{1}$$
 \mathbb{P}^{h} \mathbb{F}^{h} \mathbb{F}^{h}

Dihalocyclopropanation of E-PhCR:CHR1 (R = H, Me, R1 = Ph; R = Ph, R1 = H, Me, Et, Pr, CHMe2) with CHX3 (X = Cl, Br) and 50% aqueous NaOH containing PhCH2NEt3+ Cl- at 40-45° gave 14 title compds., thermal rearrangement of which gave mixts. of the corresponding halophenylindenes I, PhCR:CXCHR1X, Ph2C:CXCH:CR2R3 (R2 = R3 = H, Me; R2 = Me, Et, R3 = H) and/or CH2:CPhCX:CHPh. The I yield increased in the presence of acidic catalysts, and that of dienes in the presence of bases. Ph2C:CHMe and CHFBr2 gave cyclopropane II, which yielded 82% Ph2C:CFCH:CH2 on heating.

L5 ANSWER 100 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN

AN 1983:612236 CAPLUS

DN 99:212236

TI Synthesis and addition reactions of 2-phenyl-1-cyclopropene-1-carboxylates

Norden, Wolfgang; Sander, Volker; Weyerstahl, Peter

CS Inst. Org. Chem., Tech. Univ. Berlin, Berlin, D-1000, Fed. Rep. Ger.

Chemische Berichte (1983), 116(9), 3097-111

CODEN: CHBEAM; ISSN: 0009-2940

DT Journal

LA German

OS CASREACT 99:212236

GI

ΑU

SO

AB RRC:CHPh [R = Me, Ph; RR = (CH2)n (n = 3-6)] were converted into cyclopropanecarboxylic acids I and II (R1 = CO2H) via I (R1 = Cl). Spiropentane I [RR = (CH2)2, R1 = Cl] gave ethynylcyclopropane III via anionic ring cleavage with BuLi. I and II (R = CO2CMe3) gave cyclopropenes IV, but the trans isomers I reacted much faster than cis isomers II. C-3 unsubstituted chlorocyclopropanecarboxylates do not give stable cyclopropene esters even with Li dialkylamides. Addition reactions of CH2N2, thiophenolate, malonate, and CH2(CN)2 with IV were studied. Thus, e.g., IV and CH2N2 gave bicyclic pyrazolines V and VI.

- L5 ANSWER 101 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
- AN 1983:612173 CAPLUS
- DN 99:212173
- TI Reaction of 2,2-disubstituted 1-(dibromomethylene)cyclopropanes with methyllithium
- AU Kostikov, R. R.; Molchanov, A. P.; Nagi, Sh. M.
- CS Leningr. Univ., Leningrad, USSR
- SO Zhurnal Organicheskoi Khimii (1983), 19(7), 1437-44
 - CODEN: ZORKAE; ISSN: 0514-7492
- DT Journal
- LA Russian
- OS CASREACT 99:212173

GI

AB I [R,R1 = cyclopropyl (Z), Z; Ph, Me; 4-MeOC6H4, Me; 4-MeC6H4, Me; Ph, Z; 4-MeO6H4, Z; 4-ClC6H4, Z; Ph, Ph] were prepared and treated with MeLi to give RR1C:CHC.tplbond.CH (II) and/or III. Electron-donor groups on the ring of I favored formation of II, while acceptor groups favored III formation.

- L5 ANSWER 102 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
- AN 1983:495690 CAPLUS
- DN 99:95690
- TI Electroorganic reactions on organic electrodes. 4. Stereochemical studies of the electrolytic reactions of organic compounds. XXIII. Electrochemical asymmetric reduction of prochiral carbonyl compounds, oximes, and a gem-dihalide on a poly-L-valine-coated graphite electrode
- AU Abe, Shigemitsu; Fuchigami, Toshio; Nonaka, Tsutomu
- CS Grad. Sch. Nagatsuta, Tokyo Inst. Technol., Yokohama, 227, Japan
- SO Chemistry Letters (1983), (7), 1033-6 CODEN: CMLTAG; ISSN: 0366-7022
- DT Journal
- LA English
- AB The electrochem. asym. reduction of prochiral carbonyl compds., oximes, and a gem-dihalide was examined by using a poly-L-valine-coated graphite

electrode. The highest asym. yield (16.6%) was obtained in the reduction of 1,1-dibromo-2,2-diphenylcyclopropane [17343-74-7] to the corresponding monobromocyclopropane.

- L5 ANSWER 103 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
- AN 1983:215511 CAPLUS
- DN 98:215511
- TI Polyhaloallenes and -acetylenes. Part 16. Further 1,3-dipolar cycloadditions to perfluoropropadiene
- AU Blackwell, Gordon B.; Haszeldine, Robert N.; Taylor, David R.
- CS Dep. Chem., Univ. Manchester Inst. Sci. Technol., Manchester, M60 1QD, UK
- SO Journal of the Chemical Society, Perkin Transactions 1: Organic and
 - Bio-Organic Chemistry (1972-1999) (1983), (1), 1-5
- CODEN: JCPRB4; ISSN: 0300-922X DT Journal
- LA English
- OS CASREACT 98:215511
- GΙ

- Treatment of nitrones PhCH:N+(R)O- (R = Me, Et, PhCH2) with (F2C:)2C at 20° for 5 h gave isoxazolidines I (R as before) in 71, 99, and 79% yield, resp. (F2C:)2 also reacted with PhCR1:N2 (R1 = H, Ph) at 20° in C6H6 to give pyrazolines II (R1 = H, Ph) in 78 and 20% yield, resp. On heating, II (R1 = Ph) eliminated N2 to give the cyclopropane III in 15% yield. The regiospecificity of the dipolar addition reactions of (F2C:)2C are discussed in relation to frontier orbital theory.
- L5 ANSWER 104 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
- AN 1983:34001 CAPLUS
- DN 98:34001
- TI Applications of phase transfer catalysis. 23. Note on bromoiodocarbene and on pertinent halogen exchange processes
- AU Dehmlow, Eckehard V.; Broda, Witold
- CS Fak. Chem., Univ. Bielefeld, Bielefeld, D-4800/1, Fed. Rep. Ger.
- SO Chemische Berichte (1982), 115(12), 3894-7
 - CODEN: CHBEAM; ISSN: 0009-2940
- DT Journal
- LA German

GΙ

AB Halogen exchange occurred in either HCBr2I or HCBrI2 in CH2Cl2 and 50% aqueous NaOH and PhCH2NEt3+Cl-. I (R = H, Cl) was treated with either HCBr2I or HCBrI2 to give cyclopropane derivs. (e.g. II) by trapping carbene intermediates.

L5 ANSWER 105 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN

AN 1982:571159 CAPLUS

DN 97:171159

TI Stereochemistry of electroreduction of bromocyclopropanes. Part II. Stereoselectivity of electroreduction of optically active monobromocyclopropanes. Effect of electrolysis conditions

AU Hazard, Roland; Jaouannet, Serge; Raoult, Eugene; Tallec, Andre

CS Lab. Electrochim., Univ. Rennes, Rennes, 35042, Fr.

SO Nouveau Journal de Chimie (1982), 6(6), 325-33

CODEN: NJCHD4; ISSN: 0398-9836

DT Journal

LA French

OS CASREACT 97:171159

The 2-electron reduction of S (+) 1-bromo-1-carboxy-2,2-diphenylcyclopropane AB [83198-34-9] and its parent ester was studied. The ease of cleavage of the C-Br bond depends on the nature of the supporting electrolyte cation which also plays a determining role in the stereoselectivity of the reduction when performed at a Hg cathode. In aqueous acetate buffer, in the presence of NH4+, a preferential retention of configuration was observed: the more neg. the working potential, the higher the retention (a ratio of 70% was observed in the case of the ester). By contrast, the presence of R4N+ gives rise to a major inversion, the ratio of which does not depend on the working potential but increases with the bulkiness of the organic cation (the ratio of inversion is 60% in the case of the ester with Bu4N+). In ammoniacal buffer, similar results were also observed Nevertheless, the overall yield of inversion depends, in the presence of R4N+, on the applied potential. In all the cases, the interpretation of results takes into account the fact that the proton-donating ability at the electrode depends on the nature of the interface.

L5 ANSWER 106 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN

AN 1982:545003 CAPLUS

DN 97:145003

TI Chloropalladation of phenyl-substituted methylenecyclopropanes

AU Dallas, Bruce K.; Hughes, Russell P.; Schumann, Karen

CS Dep. Chem., Dartmouth Coll., Hanover, NH, 03755, USA

SO Journal of the American Chemical Society (1982), 104(20), 5380-3

CODEN: JACSAT; ISSN: 0002-7863

DT Journal

LA English

GI

 R_2C $CR^1_2R^2$ CHR^2R^3 CH_2 CH_2 CH_2 CH_2 CH_2 CH_2

AB Chloropalladation of methylenecyclopropanes with Ph groups on the cyclopropane ring involves 1,3-addition of Pd-Cl to the organic mol., with cleavage of the 2,3-σ bond of the ring. Thus, 2,2-diphenylmethylenecyclopropane in CDCl3 or C6D6 gave 1:1 I (R = Ph, R1 = H; R = H, R1 = Ph; R2 = Cl) under kinetic control; the latter isomerizes to the former. In MeOH, solvolysis of I (R = H, R1 = Ph, R2 = Cl) gave I (R2 = OMe) more rapidly than isomerization to give I (R = Ph, R1 = H, R2 = Cl). The mechanisms of isomerization and solvolysis are discussed; the kinetics of the isomerization were determined 2,2-Diphenylmethylenecyclopropane-3,3-d reacted similarly. 2-Phenylmethylenecyclopropane is chloropalladated to give II [R = R1 = H, R2 = Ph (III); R = Ph, R1 = R2 = H; R = R2 = H, R1 = Ph; R3 = Cl]; only III isomerizes to an equilibrium mixture of the other isomers in refluxing MeCN.

II

In refluxing MeOH, III solvolyzed to II (R3 = OMe) without isomerization. The mechanism of chloropalladation of phenyl-substituted methylenecyclopropanes is identical with that observed in alkyl analogs.

- L5 ANSWER 107 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
- AN 1982:492540 CAPLUS
- DN 97:92540
- TI Steric course of the substitution at the cyclopropane skeleton by cobal(I)oxime. Synthesis and characterization of cyclopropylcobaloximes
- AU Schaeffler, Juergen; Deppisch, Bertold; Retey, Janos
- CS Inst. Orq. Chem., Univ. Karlsruhe, Karlsruhe, D-7500, Fed. Rep. Ger.
- SO Chemische Berichte (1982), 115(6), 2229-41
 - CODEN: CHBEAM; ISSN: 0009-2940
- DT Journal
- LA German
- OS CASREACT 97:92540
- AB 7,7-Dibromo- (I) and exo- (II) and endo-7-bromodibenzo[b,d]norcaradiene (III) were synthesized and reacted with cobal(I)oxime. (7-Bromodibenzo[b,d]norcaradien-7-yl) (pyridine) cobaloxime was formed from I, along with (dibenzo[b,d]norcaradien-7-yl) (pyridine) cobaloxime (IV) and (dibenzo[a,c]cycloheptatrien-6-yl) (pyridine) cobaloxime, whereas the reaction of II yielded IV as the sole alkylcobaloxime. Under the same conditions III was inert. The substitution in II occurred with retention of configuration, whereas the analogous substitution in the 2 enantiomeric 1-bromo-1-methyl-2,2-diphenylcyclopropanes occurred with racemization. The observed retention was caused merely by steric effects; cyclopropyl
- L5 ANSWER 108 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN

radical intermediates occurred in both cases.

- AN 1982:438516 CAPLUS
- DN 97:38516
- TI Stereochemistry of electroreductions of bromocyclopropanes. 1-Asymmetric electrochemical synthesis by reduction at a mercury cathode in the presence of adsorbed alkaloids
- AU Hazard, R.; Jaouannet, S.; Tallec, A.
- CS Lab. Electrochim., Univ. Rennes, Rennes, 35042, Fr.
- SO Tetrahedron (1982), 38(1), 93-102
 - CODEN: TETRAB; ISSN: 0040-4020
- DT Journal
- LA English
- GΙ

- AB The asym. electrochem. reduction of cyclopropanes I (R = Br, CO2H, CO2Me) in the presence of adsorbed alkaloid cations is reported. For the reduction of I (R = Br), optical yields of <45% (-)-I (R = H) were obtained in the presence of adsorbed emetine cations. The mechanism involves preferential presentation of 1 stereotopic face of the substrate at the Hg cathode made chiral by adsorption of the alkaloid, followed by protonation of the acidic form of the inductor of the carbanion resulting from a 2-electron reduction
- L5 ANSWER 109 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
- AN 1982:423265 CAPLUS
- DN 97:23265
- TI Reaction of chloromethylcarbene with ketene alkyl silyl acetals; a new synthesis of 2-methyl-2-alkenoic esters
- AU Slougui, Nasser; Rousseau, Gerard; Conia, Jean Marie
- CS Lab. Carbocycles, Univ. Paris-Sud, Orsay, F-91405, Fr.
- SO Synthesis (1982), (1), 58-60 CODEN: SYNTBF; ISSN: 0039-7881
- DT Journal
- LA English

$$R^1$$
 OSiMe₃ OR³ I

The title reaction was described and discussed. Silylating R1R2CHCO2R3 [R1 = H, Me, Et, pentyl, CMe3, Ph, CHMeEt; R2 = H, Me, Ph; R1R2 = (CH2)4; R3 = CH2Ph, Me, Et] with Me3SiCl [LiN(CHMe2)2, THF] gave 50-91% (E)- and (Z)-R1R2C:C(OR3)OSiMe3 which cyclized with :CClMe (from Cl2CHMe and BuLi) in hexane to give diastereoisomeric cyclopropanes I. These were immediately refluxed 6 h in MeOH-NEt3 to give 32-95% (E)- and (Z)-R1R2C:CMeCO2R3.

L5 ANSWER 110 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN

AN 1982:422938 CAPLUS

DN 97:22938

TI Products and kinetic substituent effects in the reactions of diaryldiazomethanes with 2,5-dichloro-p-benzoquinone

AU Oshima, Takumi; Nagai, Toshikazu

CS Coll. Gen. Educ., Osaka Univ., Toyonaka, 560, Japan

SO Bulletin of the Chemical Society of Japan (1982), 55(2), 551-4 CODEN: BCSJA8; ISSN: 0009-2673

DT Journal

LA English

OS CASREACT 97:22938

AB (RC6H4)2CN2 (R = p-MeO, p-Me, H, p-Cl) react with 2,5-dichloro-p-benzoquinone at its conjugated C:C and C:O bonds to give bicyclic diones and poly(2,5-dichlorohydroquinone benzhydryl ethers), resp., obeying a 2nd-order rate law. The product ratios of the polyethers to the bicyclic diones increased from 1.1 to 8.1 with the electron-donating ability of the substituents. The presence of MeOH as a trapping agent stopped the polymerization completely and afforded the methanolysis product, though no essential change was found in the formation of the bicyclic dione.

L5 ANSWER 111 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN

AN 1982:180436 CAPLUS

DN 96:180436

TI Cyclopropanes. XLI. Electron transfer from lithium metal surfaces to (\pm) and (-)-(S)-1-fluoro-1-methyl-2,2-diphenylcyclopropane

AU Walborsky, H. M.; Powers, E. J.

CS Chem. Dep., Florida State Univ., Tallahassee, FL, 32306, USA

Israel Journal of Chemistry (1981), 21(2-3), 210-20

CODEN: ISJCAT; ISSN: 0021-2148

DT Journal

LA English

OS CASREACT 96:180436

GI

SO

AB The reaction of (\pm) -I with Li metal produced a variety of ring-opened, as well as cyclopropane, products. Initial electron transfer from the Li metal surface is to the Ph ring of I rather than to the C-F bond. Using chiral I, the 1-lithio-1-methyl-2,2-diphenylcyclopropane produced yielded, upon carbonation, the corresponding acid which was largely racemized. The mechanism of the electron transfer reaction is discussed.

- L5 ANSWER 112 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
- AN 1982:143001 CAPLUS
- DN 96:143001
- TI Stability and oxidative coupling of chiral vinyl- and cyclopropylcopper reagents. Formation of a novel dissymmetric diene
- AU Walborsky, H. M.; Banks, R. B.; Banks, M. L. A.; Duraisamy, M.
- CS Chem. Dep., Florida State Univ., Tallahassee, FL, 32306, USA
- SO Organometallics (1982), 1(4), 667-74
 - CODEN: ORGND7; ISSN: 0276-7333
- DT Journal
- LA English
- GI For diagram(s), see printed CA Issue.
- AB Chiral (S)-[(4-methylcyclohexylidene)methyl]- [(S)-I] and (S)-(1-methyl-2,2-diphenylcyclopropyl)copper (II) were prepared and are optically stable. Oxidative coupling of (R)-I leads to the formation of an unusual chiral 1,3-diene having biaxial dissymmetry, (+)-(aR,aR)-bis(4-methylcyclohexylidene)ethane (III), the chiroptical properties of which are reported. The thermal and dioxygen reaction of I aggregate lead to a variety of reactions other than coupling to give chiral and meso-bis(1-methyl-2,2-diphenylcyclopropane), resp. The radical
- L5 ANSWER 113 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
- AN 1982:51424 CAPLUS
- DN 96:51424
- TI Heterogeneous hydrogenation of organic halogen compounds using carrier-fixed organotin hydride
- AU Schumann, Herbert; Pachaly, Bernd
- CS Inst. Anorg. Anal. Chem., Tech. Univ., Berlin, D-1000/12, Fed. Rep. Ger.
- SO Angewandte Chemie (1981), 93(12), 1092-3 CODEN: ANCEAD; ISSN: 0044-8249

nature of the reaction was discussed.

- DT Journal
- LA German
- AB Carrier-fixed organotin hydrides were obtained by treating (MeO)3SiXSnBu2H (X = CH2CH2, MeCH) with Al2O3 and (EtO)3SiCH2CH2SSnClR2 (R = Bu, Ph) with silica gel, followed by treatment with (Me2CHCH2)2AlH. The resulting hydrides reduced MeI, BuBr, and 1,1-dichloro-2,2-diphenylcyclopropane to the corresponding hydrocarbons.
- L5 ANSWER 114 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
- AN 1981:550000 CAPLUS
- DN 95:150000
- TI Fulvenes and fulvalenes. 31. Reactions of cyclopropyllithium carbenoids with cyclopentenone
- AU Sabbioni, Gabriele; Weber, Andreas; Galli, Roberto; Neuenschwander, Markus
- CS Inst. Org. Chem., Univ. Bern, Bern, CH-3012, Switz.
- SO Chimia (1981), 35(3), 95-7
- CODEN: CHIMAD; ISSN: 0009-4293
- DT Journal
- LA German

GI

OS CASREACT 95:150000

$$R^{1}$$
 R^{2}
 R^{3}
 R^{1}
 R^{4}
 R^{2}
 R^{4}
 R^{2}
 R^{4}
 R^{2}
 R^{4}
 R^{2}
 R^{3}
 R^{2}
 R^{1}
 R^{3}
 R^{2}
 R^{4}

The attempted synthesis of 5,6-dihydrocalicenes was used to check the versatility of the addition of Li cyclopropylcarbenoids to 2-cyclopentenone. Li carbenoids, prepared by the reaction of BuLi with dihalocyclopropanes I [R1-R4 = Me; R1 = R4 = H, R2 = R3 = Ph; R1R2 = (CH2)4, R1 = Et, R2 = Me, R1R2 = CH2OCH2, R3 = R4 = H; R1 = Et, R3 = Me, R2 = R4 = H; R1 = EtO, SiMe3, PhS, MeS, R2-R4 = H], attack the carbonyl C atom of cyclopentenone as long as the substituents are small to give II (R1 = Me, EtO, Me3Si, MeS). Otherwise, the main reaction is a deprotonation of cyclopentenone to give III. The former reaction was used to prepare dihydrocalicenes IV (R1 = Et, R2 = R4 = H, R3 = Me; R1 = Me3Si, R2-R4 = H).

L5 ANSWER 115 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN

ΙV

AN 1981:549996 CAPLUS

DN 95:149996

TI The chemistry of small ring compounds. Part 43. Synthesis of 1-substituted cyclopropyl sulfides

AU Jorritsma, R.; Steinberg, H.; De Boer, T. J.

CS Lab. Org. Chem., Univ. Amsterdam, Amsterdam, 1018 WS, Neth.

SO Recueil des Travaux Chimiques des Pays-Bas (1981), 100(5), 184-94

CODEN: RTCPA3; ISSN: 0034-186X

DT Journal

LA English

OS CASREACT 95:149996

AB 1-Hydroxy- and 1-halocyclopropyl sulfides can be prepared starting from cyclopropanone. Cyclopropyl sulfides with a halogen or a dimethylsulfonium group in the α -position can be transformed into 1-substituted cyclopropyl sulfides with a variety of nucleophiles. Thus, the usual difficulties encountered with nucleophilic substitution at three-membered rings, i.e. low rates and ring opening, are largely removed by the presence of an alkylthio group at the same ring carbon atom as the leaving group.

L5 ANSWER 116 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN

AN 1981:497205 CAPLUS

DN 95:97205

TI Synthesis and ring cleavage of highly substituted 1,1-dichloro- and 1-bromo-1-fluorocyclopropanes

AU Anke, Lutz; Reinhard, Detlef; Weyerstahl, Peter

CS Inst. Org. Chem., Tech. Univ. Berlin, Berlin, D-1000/12, Fed. Rep. Ger.

Liebigs Annalen der Chemie (1981), (4), 591-602 CODEN: LACHDL; ISSN: 0170-2041

DT Journal

LA German

OS CASREACT 95:97205

GI

SO

AB In the carbene reaction of 21 tri- and tetrasubstituted olefins, most gave high yields of dihalocyclopropanes (e.g., Me2C:CMePh gave 91% I), but the highly hindered PhMeC:CPh2, (PhCH2)2C:C(CH2Ph)2, and 9,9'-bifluorenylidene did not react, and in borderline cases [e.g., (Z)-PhMeC:CMePh] ring cleavage products were observed

L5 ANSWER 117 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN

AN 1981:424102 CAPLUS

Ι

DN 95:24102

TI Experimental evidence for orbital symmetry control of stereochemistry in some (methylenecyclopropane)iron-carbonyl reactions

AU Pinhas, Allan R.; Samuelson, Ashoka G.; Risemberg, Rafael; Arnold, Edward V.; Clardy, Jon; Carpenter, Barry K.

CS Dep. Chem., Cornell Univ., Ithaca, NY, 14853, USA

SO Journal of the American Chemical Society (1981), 103(7), 1668-75

CODEN: JACSAT; ISSN: 0002-7863

DT Journal

LA English

AB The reactions of I[R = H(II), Rh(III)] with Fe-CO reagents are observed The stereochem. of ring opening of II to (1-phenyltrimethylenemethane) iron tricarbonyl is determined by stereospecific D-labeling. The D-labeling also allows information to be gained about the conversion of II to [(E)-1-phenylbutadiene]iron tricarbonyl. An Fe(CO)4 complex obtained from the reaction of III with Fe2(CO)9 is identified crystallog.; this compound is a plausible intermediate in the formation of (1,1-diphenyltrimethylenemethane)iron tricarbonyl. A general mechanism, which is consistent with the stereochem. predictionsbased on frontier MO symmetry considerations, is presented for all these reactions. This mechanism is also an alternative for the reaction of Fe2(CO)9 with methylenecyclopropane.

L5 ANSWER 118 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN

1981:208399 CAPLUS

DN 94:208399

TI Reaction of 1,1-difluorocyclopropanes with organolithium compounds

AU Suda, Minoru

CS Sagami Chem. Res. Cent., Kanagawa, 229, Japan

SO Tetrahedron Letters (1980), 21(45), 4355-8

CODEN: TELEAY; ISSN: 0040-4039

DT Journal

LA English

OS CASREACT 94:208399

GI

AN

- Substituted 1,1-difluorocyclopropanes reacted with organolithium reagents to give either cyclopropenes or monosubstituted acetylenes depending on the substituents on the cyclopropane ring. E.g., difluorocyclopropanes I [R = Ph, R1 = R2 = H; RR1 = (CH2)6, R2 = H] reacted with MeLi to give the cyclopropenes II [R = Ph, R1 = H; RR1 = (CH2)6,], whereas I (R = Ph, R1 = H, R2 = Me, Ph) reacted with BuLi to give PhC(Bu)(R)C.tplbond.CH (R = Me, Ph, resp.). The mechanism of the transformations are discussed.
- L5 ANSWER 119 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN

AN 1981:203791 CAPLUS

DN 94:203791

TI Structure-activity relationships of DDT-type analogs based on in vivo toxicity to the sensory nerves of the cockroach, Periplaneta americana L

AU Brown, Daniel D.; Metcalf, Robert L.; Sternburg, James G.; Coats, Joel R.

CS Dep. Entomol., Univ. Illinois, Urbana, IL, 61801, USA

SO Pesticide Biochemistry and Physiology (1981), 15(1), 43-57

CODEN: PCBPBS; ISSN: 0048-3575

DT Journal

LA English

- AB Forty-three DDT [50-29-3]-type compds. were applied in saline suspension to the crural nerve of P. americana and the threshold concentration (ED50) to produce trains of impulses was determined together with the frequency of appearance of repetitive afterdischarge. These quant. neurol. measures were evaluated in multiple regression analyses of structural parameters including van der Waal's volume, the F and R components of Hammet's σ , and the hydrophobic constant Π . This structure-activity anal. provides an accurate estimation of the intrinsic toxicity of the DDT analogs. The results affirm previous working theories that the bulk of the functional groups within the DDT framework is the primary factor relating to activity; however, conformation is also an important parameter.
- L5 ANSWER 120 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN

AN 1981:174160 CAPLUS

DN 94:174160

- TI Conformation of bis(p-chlorophenyl)- β -trichloroethane and some of its analogs in solutions
- AU Arbuzov, B. A.; Timosheva, A. P.; Vul'fson, S. G.; Karelov, A. A.; Vereshchagin, A. N.
- CS Inst. Org. Fiz. Khim. im. Arbuzova, Kazan, USSR
- SO Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya (1981), (1), 124-7

CODEN: IASKA6; ISSN: 0002-3353

DT Journal

LA Russian

GΙ

- AB The dipole moments and Kerr consts. of Cl3CCH(C6H4R-4)2 (R = H, Me, Cl, Br) indicated that the aliphatic C-H bond was eclipsed by one of the aryl rings and that the other ring made an angle of 85° with the CAr-C-CAr plane. DDT and I had similar conformations.
- L5 ANSWER 121 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN

AN 1981:174031 CAPLUS

DN 94:174031

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An extension of the linear relationship between molecular rotation and
ΤI
     bond refraction
ΑU
     Poh, Bo-Long
     Sch. Chem. Sci., Univ. Sains Malaysia, Penang, Malay.
CS
     Australian Journal of Chemistry (1980), 33(7), 1409-17
SO
     CODEN: AJCHAS; ISSN: 0004-9425
DТ
     Journal
```

LA English

For the empirical equations $[M]D = m\Sigma RD + I$; [M]D is the mol. AB rotation, ERD is the sum of bond refractions, and m and I are consts. for a given series of compds., a different treatment of the term ERD extends the usefulness of the equation to all types of substituents, not just monovalent and linear substituents.

ANSWER 122 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN L5

AN 1981:46648 CAPLUS

DN . 94:46648

Electroreduction of optically active 1-bromo-1-carbomethoxy-2,2-TI diphenylcyclopropane: factors influencing stereoselectivity

ΑU Jaouannet, S.; Hazard, R.; Tallec, A.

CS Lab. Electrochim., Univ. Rennes, Rennes, 35042, Fr.

Journal of Electroanalytical Chemistry and Interfacial Electrochemistry (SO **1980**), 111(2-3), 397-400 CODEN: JEIEBC; ISSN: 0022-0728

DTJournal LA English

 $Ph \frac{1}{\sqrt{2}} CO_2 Me$

GΙ

AB The stereoselectivity in the reduction of (+)(S)-I (R = Br) to give varying amts. of (-)(R)-I(R=H) depended on the composition of the supporting electrolyte and the value of the elec. potential used. The proton-donating ability of the supporting electrolite is important; the faster the protonation, the higher the percentage of retention of configuration.

ANSWER 123 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN L5

AN 1981:46643 CAPLUS

DN 94:46643

Magnetic and other field effects on prochiral chemical reactions TI

Piotrowska, Krystyna; Edwards, Deborah; Mitch, Alan; Dougherty, Ralph C. ΑU

CS Dep. Chem., Florida State Univ., Tallahassee, FL, 32306, USA

so Naturwissenschaften (1980), 67(9), 442-5 CODEN: NATWAY; ISSN: 0028-1042

DTJournal

LA English

AB Expts. are reported in which 3 prochiral organic reactions were conducted in the presence of a .apprx.1T magnetic field which was oriented with reference to the earth's geometric axes. The sign and magnitude of the rotation varied with the macroscopic orientation of the magnetic field and the time that the reaction was performed. Control measurements were in accord with expectations. The fact that the sign of the observed optical rotation of the product was reversed for all 3 reported reactions when the magnetic field was reversed for reactions conducted on the same day suggests that either the observed asym. synthesis was due to the reactions being conducted in a chiral phys. field or extremely unusual stochastic processes were involved.

ANSWER 124 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN L5

1980:638232 CAPLUS AΝ

DN

TI Addition of diphenylmethylene to 1,2-dichloroethylenes. New chemical

evidence for a carbene singlet-triplet equilibrium Gaspar, Peter P.; Whitsel, Bonnie L.; Jones, Maitland, Jr.; Lambert, ΑU Joseph B. Dep. Chem., Washington Univ., St. Louis, MO, 63130, USA CS Journal of the American Chemical Society (1980), 102(19), SO CODEN: JACSAT; ISSN: 0002-7863 DT Journal LA English Addition of diphenylmethylene to cis- and trans-1,2-dichloroethylene gives AB the corresponding 1,2-dichloro-3,3-diphenylcyclopropane with greater than 90% stereospecificity. A product of addition with rearrangement, 3,3-dichloro-1,1-diphenyl-1-propene, is also obtained; this is the major product from trans olefin. The cyclopropane product arises principally from concerted addition by the singlet carbene, while the rearrangement product is assigned to the triplet carbene. Neither competition from another olefin nor moderation by hexafluorobenzene alters the product ration from addition of diphenylmethylene to dichloroethylenes, thus, establishment of a singlet-triplet equilibrium for diphenylmethylene under the conditions employed for olefin addition reactions is suggested. L5 ANSWER 125 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN ΑN 1980:619968 CAPLUS DN 93:219968 Liquid chromatography on triacetylcellulose. 3. Liquid chromatography of ΤI enantiomers: determination of enantiomer purity in spite of peak overlapping ΑU Mannschreck, Albrecht; Mintas, Mladen; Becher, Georg; Stuehler, Georgine CS Inst. Chem., Univ. Regensburg, Regensburg, D-8400, Fed. Rep. Ger. SO Angewandte Chemie (1980), 92(6), 490-1 CODEN: ANCEAD; ISSN: 0044-8249 DTJournal LA German GΙ CHRCOCMe₃ Ι

AB Using the title liquid chromatog, method, the enantiomeric purities of (R-)-I (R = p-ClC6H4O), (S)-(HOCH2CBr:CBr)2, and (R)-1-bromo-2, 2diphenylcyclopropane samples were ≤87, 29, and, 71%, resp.

ANSWER 126 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN L5

ΑN 1980:585618 CAPLUS

DN93:185618

TIAlternative pathways in the reactions of cyclopropyl halides with alkali metal naphthalenes

ΑU Boche, G.; Schneider, D. R.; Wintermayr, H.

CS Inst. Org. Chem., Univ. Muenchen, Munich, D-8000/2, Fed. Rep. Ger.

SO Journal of the American Chemical Society (1980), 102(17), 5697-9 CODEN: JACSAT; ISSN: 0002-7863

DΤ Journal

LA English

GI

$$R$$
 Me
 I

Cyclopropyl halides with good electron-accepting substituents (e.g., I; R AB = Ph or R2 = 2,2'-biphenylene; X = halo) react with alkali metal

naphthalenes in THF or (MeOCH2)2 to give the corresponding cyclopropanes with net retention of configuration. The retention is not due to the successful competition of electron transfer to and inversion of the intermediate cyclopropyl radicals, as suggested earlier by J. Jacobus and D. Pensak (1969). Rather, the inversion of secondary and tertiary cyclopropyl radicals is much faster ($k \ge 109 \text{ s-1}$; ΔG .thermod. 3.7 kcal-mol-1) than electron transfer from naphthalene radical anions.

- L5 ANSWER 127 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
- AN 1980:420664 CAPLUS
- DN 93:20664
- TI Insect sensory nerve potentials: effects of insecticides
- AU Holan, G.; Poppleton, B. J.; Spurling, T. H.; Virgona, C. T.
- CS Div. Appl. Org. Chem., CSIRO, Melbourne, 3001, Australia
- SO Insect Neurobiol. Pestic. Action, Proc. Soc. Chem. Ind. Symp. (
 1980), Meeting Date 1979, 73-8 Publisher: Soc. Chem. Ind., London,
 Engl.
 - CODEN: 42YIA8
- DT Conference
- LA English
- AB Electrophysiol. studies were made on the isolated labellar hair of the blowfly (Luncilia cuprina) treated with insecticides. The spike-potential multiplicity index (Holan, G., 1975) vs. threshold curves differed for pyrethroid-DDT compds., such as 4-ethoxyphenyl-1-(3-phenoxybenzyl)-2,2-dichlorocyclopropanecarboxylate, as compared to DDT-type compds., such as 2,2-bis(4-ethoxyphenyl)-3,3-dimethyloxetane [32795-78-1]. The 2 groups of insecticides act by different mechanisms. Computer-generated models were produced for simulated nerve spike trains.
- L5 ANSWER 128 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
- AN 1979:574923 CAPLUS
- DN 91:174923
- TI Synthesis and properties of 1,1-diiodo- and 1-iodo-1-x-cyclopropanes
- AU Mathias, Rolf; Weyerstahl, Peter
- CS Inst. Org. Chem., Tech. Univ. Berlin, Berlin, D-1000/12, Fed. Rep. Ger.
- SO Chemische Berichte (1979), 112(9), 3041-53 CODEN: CHBEAM; ISSN: 0009-2940
- DT Journal
- LA German
- OS CASREACT 91:174923
- AB 1,1-Diiodo-2-phenylcyclopropane (I) underwent Grignard reaction with acetone to give α,α -dimethyl-2-phenylcyclopropanemethanol (with complete elimination of iodine) or with EtBr to give chiefly 1-iodo-1-phenylcyclopropane isomers, and it reacted with LiCuR2 (R = Me, Bu, Ph or vinyl) to give the corresponding 1-hydrocarbyl-1-iodo-2-phenylcyclopropane. The iodine atom was similarly replaced in reactions of 1-halo-1-iodo-2-phenylcyclopropanes. With 4-MeC6H4SO3Ag or (AcO)2Hg, I was cleaved to give products arising from the resultant allyl cation.
- L5 ANSWER 129 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
- AN 1979:574858 CAPLUS
- DN 91:174858
- TI Electrochemical asymmetric synthesis. Reduction of 1,1-dibromo-2,2-diphenylcyclopropane
- AU Hazard, R.; Jaouannet, S.; Tallec, A.
- CS Lab. Electrochim., Univ. Rennes, Rennes, Fr.
- SO Tetrahedron Letters (1979), (13), 1105-8 CODEN: TELEAY; ISSN: 0040-4039
- DT Journal
- LA French

GI

- AB Cyclopropane I (R = Br) underwent electrochem. debromination at the sp3 prochiral C atom, in the presence of strychnine or emetine adsorbed at a Hg cathode at pH 4.7 and 9.7, to give (-)(R)-I (R = H) as the major product. In the presence of adsorbed yohimbine in acetate buffer at pH 4.7 electrochem. asym. reduction of I (R = Br) gave (+)(S)-I (R = H).
- L5 ANSWER 130 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN

AN 1979:456025 CAPLUS

DN 91:56025

TI Thermal isomerization of arylmethylenecyclopropanes to indenes: the question of orbital symmetry control as a factor in hydrogen transport

AU Gilbert, J. C.; Kurzawa, F.

CS Dep. Chem., Univ. Texas, Austin, TX, 78712, USA

SO Journal of Organic Chemistry (1979), 44(13), 2123-6

CODEN: JOCEAH; ISSN: 0022-3263

DT Journal

LA English

AB Examination of the D distribution of the 2-methyl-3-phenylindene resulting from rearrangement of 2-phenyl-2-(perdeuteriophenyl)methylene cyclopropane demonstrates conclusively that orbital symmetry does not control the net 1,7-H migration required to produce the indene. An alternative explanation is offered for the necessity of having diaryl substitution at C-2 of the methylenecyclopropane in order to observe the isomerization.

- L5 ANSWER 131 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
- AN 1979:455808 CAPLUS

DN 91:55808

- TI Electrocyclic ring opening of cyclopropyl halides in the course of their reaction with sodium iodide in acetone
- AU Luckenbach, Reiner; Mueller, Nikolaus
- CS Org.-Chem. Inst., Univ. Mainz, Mainz, Fed. Rep. Ger.
- SO Zeitschrift fuer Naturforschung, Teil B: Anorganische Chemie, Organische Chemie (1979), 34B(3), 464-80
 CODEN: ZNBAD2; ISSN: 0340-5087
- DT Journal
- LA German

GΙ

Ph Br II OMe III

AB Reaction of cyclopropyl halides (e.g., I-III) with NaI in Me2CO (i.e. under typical SN2-conditions), proceeded via ring opening to allylic systems finally yielding 1,5-hexadienes on dimerization; ring-retained products were not detected. Woodward-Hoffman rules indicate a cationic synchronous mechanism. The kinetic data fit the Hammett equation using $\sigma\text{-values}$ for cyclopropyl bromides and $\sigma\text{+-values}$ for geminal cyclopropyl dichlorides, resp. The validity of the Woodward-Hoffmann-De Puy rule (according to which in synchronous reactions leaving groups situated endo are strongly favored over those situated exo) was tested in corresponding expts. involving condensed ring systems.

- L5 ANSWER 132 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
- AN 1979:404980 CAPLUS
- DN 91:4980
- TI Multiple bond activity in the adamantane ring in a reaction with dichlorocarbene
- AU Kostikov, R. R.; Grishina, E. N.; Slobodin, Ya. M.
- CS Sev.-Zapadn. Zaochn. Politekh. Inst., Leningrad, USSR
- SO Zhurnal Organicheskoi Khimii (1979), 15(2), 331-6 CODEN: ZORKAE; ISSN: 0514-7492

- AB Reaction of methyleneadamantane I (R1 = H, Me, Et, Me2CH, Me2CHCH2, Ph; R2 = H, Me, Ph) with :CCl2 gave 40-67% II. Similarly, treatment of diadamantylidene with : CCl2 gave 9% III. Spiro compds. IV (R1 = R2 = Me, Ph) were prepared similarly from the appropriate methylenecyclohexanes. The IR and NMR of II, III and IV were tabulated. The rate consts. of the reaction of R2C:CR1R2 (R2 = 2-adamantylidene, (CH2)5; R = Me, H; R1 = H, Me, Ph; R2 = H, Me, Et, Me2CH, Me2CHCH2, Ph, Me) with :CCl2 were determined
- L5 ANSWER 133 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
- AN 1979:163290 CAPLUS
- DN 90:163290
- TI Influence of temperature on the toxicity of insecticides to susceptible and resistant house flies
- AU DeVries, Donald H.; Georghiou, George P.
- CS Dep. Entomol., Univ. California, Riverside, CA, USA
- SO Journal of Economic Entomology (1979), 72(1), 48-50
- CODEN: JEENAI; ISSN: 0022-0493
- DT Journal
- LA English
- The influence of posttreatment temperature on the toxicity of 6 insecticides was investigated on a susceptible and 2 resistant strains of Musca domestica. The toxicity of dimethoate [60-51-5], parathion [56-38-2], and Isolan [119-38-0] was unaffected by temperature within the range of 15-25°. Bioresmethrin [28434-01-7], lindane [58-89-9] and CP 47412 (1,1-di(p-chlorophenyl)-2,2-dichlorocyclopropane) [3575-15-3] manifested greater toxicity at 15°. This effect was more pronounced in the resistant strains but did not reduce resistance more than 1.6-fold. Apparently, temperature within the range tested has no influence on potential resistance in the field.
- L5 ANSWER 134 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
- AN 1979:86832 CAPLUS
- DN 90:86832
- TI Selective reduction of organic halides and α -diketones by MoH2(η -C5H5)2
- AU Nakamura, Akira
- CS Fac. Sci., Osaka Univ., Toyonaka, Japan
- SO Journal of Organometallic Chemistry (1979), 164(2), 183-92 CODEN: JORCAI; ISSN: 0022-328X
- DT Journal
- LA English
- GI

As systematic study of reaction of organic halides with MoH2Cp2 (Cp = η 5-C5H5) was performed and the results were compared with those of WH2Cp2, MoH4(dppe)2 (dppe = 1,2-bis(diphenylphosphino)ethane), and FeH2(dppe)2. Among many organic halides, I was reduced stereoselectively by MoH2Cp2 to the monobromo stage. The reaction mechanism was studied with optically active PhCH(Cl)CO2Et and also with addition of some radical reagents to reveal a radical-chain mechanism. Selective reduction of α -dicarbonyl compds., e.g., I, to the α -ketol was effected by MoH2Cp2. A similar radical mechanism is proposed for this novel reaction.

L5 ANSWER 135 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN

AN 1979:86307 CAPLUS

DN 90:86307

TI Reaction of dichlorocarbene with phenyl-substituted ethylenes

AU Kostikov, R. R.; Drygailova, E. A.; Morzhakova, T. M.; Ogloblin, K. A.

CS USSI

SO Vestnik Leningradskogo Universiteta, Seriya 4: Fizika, Khimiya (
1978), (3), 114-19
CODEN: VLUFBI; ISSN: 0024-0826

DT Journal

LA Russian

AB The relative reactivity of the title olefins toward Cl2C: decreased in the order Ph2C:CH2 > PhCH:CH2 > (E)-PhCMe:CHPh > Ph2C:CHMe > (E)-PhCH:CHPh .apprx. Ph2C:CMe2. Tetrasubstituted ethylenes did not react. A correlation of the relative reactivity with the free valence index was noted.

L5 ANSWER 136 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN

AN 1979:71791 CAPLUS

DN 90:71791

TI Synthesis and reactions of 1-chloro-1-cyclopropanecarboxylic acids and 1-cyclopropene-1-carboxylic acids

AU Sander, Volker; Weyerstahl, Peter

CS Inst. Org. Chem., Tech. Univ. Berlin, Berlin, Fed. Rep. Ger.

Chemische Berichte (1978), 111(12), 3879-91

CODEN: CHBEAM; ISSN: 0009-2940

DT Journal

LA German

OS CASREACT 90:71791

GΙ

AB

SO

$$R^2$$
 R^1 Ph $C1$ Ph R^2 R^1 $C0_2$ R^2 R^1 R^2 R^2 R^1 R^2 R^2

Cyclopropanecarboxylic acids I (R = H) [R1 and R2 (the same or different) are H, Me, Ph, cyclopropyl; R3 = H, Ph] were prepared by lithiating

1,1-dichlorocyclopropanes, followed by carboxylation with CO2. I (R = Me, CMe3) were obtained by esterification. I (R = CMe3; R1 = H, Me; R2 = R3 = H) reacted with KOCMe3 to give II (R1 = H, Me). Reaction of I (R = CMe3; R1 = R2 = Me, Ph; R3 = H) with KOCMe3 gave III, which were hydrogenated to the corresponding cyclopropanes.

L5 ANSWER 137 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN

AN 1978:524490 CAPLUS

DN 89:124490

TI Structural and biological link between pyrethroids and DDT in new insecticides

AU Holan, G.; O'Keefe, D. F.; Virgona, C.; Walser, R.

CS Div. Appl. Org. Chem., CSIRO, Melbourne, Australia

SO Nature (London, United Kingdom) (1978), 272 (5655), 734

CODEN: NATUAS; ISSN: 0028-0836

DT Journal

LA English

GI

$$\begin{array}{c|c} \text{CO}_2\text{CH}_2 & \\ \hline \\ \text{C1} & \text{OPh} \end{array}$$

Based on the structural model of a nerve membrane receptor for DDT-type AB insecticides, compds. combining the structural features of both DDT and pyrethroid insecticides were synthesized and found to be active insecticides in houseflies and blowflies (Lucilia cuprina). The structural similarity and biol. properties (e.g. contact repellency values) of these compds., e.g. (±)-3'-phenoxybenzyl-p-ethoxyphenyl-2,2dichlorocyclopropanecarboxylate (I) [63935-32-0] LD50 0.19 μg, related them to both classes of insecticides. The isomer of I was 50- to 60-fold less active than I. In general, esters broadly followed DDT-analog substitution patterns in the aryl ring and the cyclopropane parts of the acid component, whereas the alc. radicals followed the activities for the same components in the pyrethroids, though exceptions were observed E.g., difluorocyclopropanes, inactive in the DDT series, possessed high activity in the combined form. There was no correlation between the partition coeffs. and the biol. activities of the compds. Low mammalian toxicity was indicated in studies with I. Development of a new range of safe insecticides is, therefore, possible.

L5 ANSWER 138 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN

AN 1978:508226 CAPLUS

DN 89:108226

TI Decarboxylation reaction. VIII. Reaction of electron-deficient carbon-carbon double bonds with trichloroacetic acid. A unique 1,1-dichlorocyclopropane formation through β -trichloromethylation

AU Nanjo, Katsumi; Suzuki, Kunio; Sekiya, Minoru

CS Shizuoka Coll. Pharm., Shizuoka, Japan

SO Chemical & Pharmaceutical Bulletin (1978), 26(3), 848-52

CODEN: CPBTAL; ISSN: 0009-2363

DT Journal

LA English

OS CASREACT 89:108226

GI

Decarboxylative cycloaddn. of CCl3CO2H (I) to R1R2C:CRCN [R = CN, CO2Et, Bz, SO2Ph; R1 = Ph, Et, Me2CH; R2 = H, Me, Et, Bu, Ph; R1R2 = (CH2)4, (CH2)5] in ether or THF in the presence of NEt3 gave II. The same reaction of I with PhCH:CR3R4 (R3, R4 = CN, CN; CN, SO2Ph; H, NO2; resp.) gave PhCH(CCl3)CHR3R4. A mechanism involving β -trichloromethylated intermediate is postulated.

L5 ANSWER 139 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN

AN 1978:121030 CAPLUS

DN 88:121030

TI Cyclic peroxides. 60. Prostanoid endoperoxide model compounds:

preparation of 1,2-dioxolanes from cyclopropanes

AU Adam, Waldemar; Birke, Arnoldo; Cadiz, Carlos; Diaz, Simon; Rodriguez, Augusto

CS Dep. Chem., Univ. Puerto Rico, Rio Piedras, P. R.

SO Journal of Organic Chemistry (1978), 43(6), 1154-8

CODEN: JOCEAH; ISSN: 0022-3263

DT Journal

LA English

GI

1,2-Dioxolanes I (R = Ph, R1 = Ph, Me, H; R = 4-BrC6H4, R1 = Me, H), potential intermediates for prostanoid endoperoxide model compds., were prepared by successive cyclization of CHCl3 with Ph2C:CH2, PhCMe:CH2, PhCH:CH2, NaOH, and methyltricaprylammonium chloride phase-transfer catalysis (51-80% yield), reduction of the dichlorocyclopropane II (R = Ph, R1 = Ph, Me, H, R2 = Cl) with Na-Me3COH in THF (40-84% yields), and hydroperoxybromination of II (R, R1 the same, R2 = H) with H2O2 and N-bromosuccinimide or 1,3-dibromo-5,5-dimethylhydantoin to give 68-87% II (R = 4-BrC6H4, R1 = Me, H, R2 = H) and 50-85% RR1C(OOH)CH2CH2Br (R, R1 as for I), which was cyclized with Ag2O to give I.

L5 ANSWER 140 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN

AN 1978:37290 CAPLUS

DN 88:37290

TI Synthesis of spatially shielded 3,3-disubstituted cyclopropenes

AU Bovin, N. V.; Surmina, L. S.; Yakushkina, N. I.; Bolesov, I. G.

CS Mosk. Gos. Univ., Moscow, USSR

SO Zhurnal Organicheskoi Khimii (1977), 13(9), 1888-94

CODEN: ZORKAE; ISSN: 0514-7492

DT Journal

LA Russian

GI



Treatment of CH2:CR1R2 (R1,R2 given; Ph, Ph; Me, Ph; Me, p-MeOC6H4; Ph, morpholino; Me, Me) with :CBr2 gave 45-84% I (R3 = Br), which were reduced by Bu3SnH or LiAlH4 to give 66-90% I (R3 = H). I (R3 = H) were dehydrobrominated to give 47-80% cyclopropenes II.

L5 ANSWER 141 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN

AN 1978:6061 CAPLUS

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DN 88:6061
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TI Reaction of dihalocarbenes with aromatic azomethines

AU Kostikov, R. R.; Khlebnikov, A. F.; Ogloblin, K. A.

CS Leningr. Gos. Univ., Leningrad, USSR

SO Zhurnal Organicheskoi Khimii (1977), 13(9), 1857-71

CODEN: ZORKAE; ISSN: 0514-7492

DT Journal

LA Russian

GΙ

$$\mathbb{R}^{\frac{1}{2}} \mathbb{R}^{\frac{1}{2}} \mathbb{R}^{2}$$

The relative rate consts. and stereochem. of the cycloaddn. of XYC: (X, Y = F, Cl, Br) to RC6H4N:CR1C6H4R2 (R = H, 4-MeO, 3-MeO, 4-Me, 4-Cl, 3-Br; R1 = H, Me, Et, Me2CH, Me3C; R2 = H, 4-MeO, 3-MeO, 4-Me, 4-Cl, 3-Cl, 3-EtO, 3-Me3CO) were studied. NMR, IR, and UV data of the aziridine products (I) were given. Linear free energy relations obtained by varying R or R2 yielded ρ values having magnitudes <0.1. In cases where X \neq Y, the tendency for a halogen atom to become located syn to the unshared electrons on the N increased in the order Br < Cl < F. MO calcns. indicated that a π approach of the carbene to the N:C bond was preferred.

L5 ANSWER 142 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN

AN 1977:452893 CAPLUS

DN 87:52893

TI Chain elongation of alkenes via gem-dihalocyclopropanes:

1,1-diphenyl-2-bromo-3-acetoxy-1-propene

AU Sandler, Stanley R.

CS Chem. Div., Borden, Inc., Philadelphia, PA, USA

Organic Syntheses (1977), 56, 32-5

CODEN: ORSYAT; ISSN: 0078-6209

DT Journal

LA English

GT

so

AB Treatment of Ph2C:CH2 with CHBr3-KOCMe3 in pentane at 0-25° gave cyclopropane I, which when treated with AgOAc in HOAc at 100-20° gave 72% Ph2C:CBrCH2OAc. Similarly ring expansion of cyclopentene gave II (R = OH, Br); the product depended on the conditions for dibromocyclopropane ring opening. PhCH:CBrCH2OAc was also obtained from styrene. Five addnl. examples were given.

L5 ANSWER 143 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN

AN 1977:422629 CAPLUS

DN 87:22629

TI Reactions of 1-chloro-2-phenyl-1-cyclopropenes

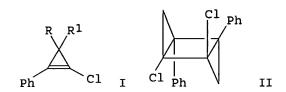
AU Henseling, Karl Otto; Quast, Dietrich; Weyerstahl, Peter

CS Inst. Org. Chem., Tech. Univ. Berlin, Berlin, Fed. Rep. Ger.

SO Chemische Berichte (1977), 110(3), 1027-33

CODEN: CHBEAM; ISSN: 0009-2940

DT Journal



1-Chloro-2-phenyl-1-cyclopropene (I; R = R1 = H) in benzene at room temperature for 48 h gave 4% the dimer II along with polymeric material. I (R = H, R1 = Me) with KOMe in MeOH gave 24% MeCH:CPhCH(OMe)2. I which are disubstituted at C(3) reacted differently, e.g., I (R,R1 = Me, Me; Me, Ph; Ph, Ph) in benzene gave PhC.tplbond.CCMe:CH2 100, PhC.tplbond.CCPh:CH2 70, or PhC.tplbond.CCPh2OH 12%, resp. The results were interpreted in terms of the stability of the cation PhC.tplbond.CC+RR1.

L5 ANSWER 144 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN

AN 1977:189253 CAPLUS

DN 86:189253

TI The reduction of qem-dichlorocyclopropanes with lithium aluminum hydride

AU Kusuyama, Yoshiaki; Ikeda, Yoshitsugu

CS Dep. Chem., Wakayama Univ., Wakayama, Japan

SO Nippon Kagaku Kaishi (1977), (2), 290-2

CODEN: NKAKB8; ISSN: 0369-4577

DT Journal

LA Japanese

AB Gem-dichlorocyclopropanes were easily reduced by LiAlH4 in boiling THF to afford cis-trans mixts. of the corresponding monochlorocyclopropanes. Relatively high isomer ratios were obtained for the reduction of (2,2-dichlorocyclopropyl)benzene and 7,7-dichloronorcarane in which a H in the substituent is close to the cis-Cl. The reduction proceeds via a synfacial mechanism in which the attacking hydride and the Cl attacked are on the same side of the cyclopropane plane.

L5 ANSWER 145 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN

AN 1977:139442 CAPLUS

DN 86:139442

TI Synthesis, ring cleavage reactions, and halogen/lithium exchange of 1-bromo-1-fluorocyclopropanes

AU Mueller, Christian; Stier, Fritz; Weyerstahl, Peter

CS Inst. Org. Chem., Tech. Univ. Berlin, Berlin, Fed. Rep. Ger.

Chemische Berichte (1977), 110(1), 124-37

CODEN: CHBEAM; ISSN: 0009-2940

DT Journal

SO

GΙ

LA German

OS CASREACT 86:139442

F Br R

The bromofluorocyclopropanes I [R = H, R1 = Me3C, Ph0, Ph (II); R = Me, R1 = Me, H2C:CMe, Ph (III); or R = R1 = Et] underwent ring cleavage reactions. II with AcOAg or PhONa gave (Z)-PhCH:CFCH2OR2 (R2 = Ac, Ph) and (Z)-PhCH:CFCH2Br in the case of the PhONa. Cleavage of 1-bromo-1-fluorotetramethylcyclopropane (IV) with di-Et malonate gave Me2C:CFCMe2CH(CO2Et)2. II with PhLi gave phenylallene and PhCH2C.tplbond.CH and with MeLi gave phenylallene and PhCHMeC:CH. II,

III, and IV with BuLi at below -105° underwent selective Br/Li exchange to give, after carboxylation and esterification, 1-fluorocyclopropanecarboxylates. The reaction at from -90 to -100° gave complex mixts.

L5 ANSWER 146 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN

AN 1976:559482 CAPLUS

DN 85:159482

TI Basic behavior of epoxides in the presence of halide ions, IV. gem-Difluorocyclopropanes from chlorodifluoromethane and alkoxide ions at low concentration

- AU Kamel, Mona; Kimpenhaus, Wolfgang; Buddrus, Joachim
- CS Natl. Res. Cent., Cairo, Egypt
- SO Chemische Berichte (1976), 109(7), 2351-69

CODEN: CHBEAM; ISSN: 0009-2940

- DT Journal
- LA German
- AB Gem-difluorocyclopropanes (14) were prepared by treatment of reactive alkenes with difluorocarbene generated by reaction of ClCHF2 with alkoxides at low concns. The latter were formed by treatment of epoxides (oxirane or epichlorohydrin) with halides (e.g., from Bu4N+Cl-). With less reactive alkenes, products from the reaction of the carbene with alcs. (from the epoxides) were also formed.
- L5 ANSWER 147 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
- AN 1976:524029 CAPLUS
- DN 85:124029
- TI Transformation of 2,3-diazabicyclo[3.1.0]hex-2-enes into 1,3-butadienes
- AU Welter, W.; Regitz, M.
- CS Fachbereich Chem., Univ. Kaiserslautern, Kaiserslautern, Fed. Rep. Ger.
- SO Tetrahedron Letters (1976), (18), 1473-6
- CODEN: TELEAY; ISSN: 0040-4039
- DT Journal
- LA German

GΙ

- Ph P(O) (OMe) 2 Ph R R P(O) (OMe) 2 Ph R Me II
- AB Photolysis of the 2,3-diazabicyclo[3.1.0]hex-2-enes I (R = Me, CMe3) gave Ph2C:CHCMeRC(:N2)P(O) (OMe)2 which reacted further to give the bicyclo[1.1.0]butanes II; in the presence of Ph2CO sensitizer Ph2C:CHC(:CMeR)P(O) (OMe)2 (III) was formed. Thermolysis of I at ≥150° gave III, Ph2C:CHCR:CMeP(O) (OMe)2, and Ph2C:CHCMe:CRP(O) (OMe)2. The butadienes were formed via the carbene :C[P(O) (OMe)2]CMeRCH:CPh2.
- L5 ANSWER 148 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
- AN 1976:523683 CAPLUS
- DN 85:123683
- TI Stereospecific deoxydichlorocyclopropanation of epoxides by dichlorocarbene generated in an emulsifying system
- AU Tabushi, I.; Kuroda, Y.; Yoshida, Z.
- CS Dep. Pharm. Sci., Kyushu Univ., Fukuoka, Japan
- SO Tetrahedron (1976), 32(9), 997-1000 CODEN: TETRAB; ISSN: 0040-4020
- DT Journal
- LA English

GI

The epoxides I [R = Ph, Me(CH2)n,n = 7,9, R1 = R2 = H; R = Ph, R1 = Me, R2 = H; R = Ph, R1 = H, R2 = Me; R = H, R1 = Ph, R2 = Me; RR1 = (CH2)4, R2 = H] underwent reaction with :CCl2, generated in an emulsifying system, to give the corresponding dichlorocyclopropene derivs. II. The reaction of cis- and trans- β -methylstyrene oxide (I; R = Ph, R1 = Me, R2 = H; R = Ph, R1 = H, R2 = Me, resp.) showed the reaction to be stereospecific, giving 95% cis-II and >96% trans-II, resp. Styrene oxide (I; R = Ph, R1 = R2 = H) gave II and PhCH:CH2; the concentration of the latter was nearly constant during the reaction. Further, the competitive reaction of α - and trans- β -methylstyrene oxide (I; R = H, R1 = Ph, R2 = Me; R = Ph, R1 = H, R2 = Me, resp.) showed that introduction of an addnl. Me group at the α -position accelerated the reaction only 12 times. The reaction involves two steps, namely deoxygenation and dichlorocyclopropanation, both of which are stereospecific and practically concerted.

L5 ANSWER 149 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN

AN 1976:494027 CAPLUS

DN 85:94027

TI Insecticidal dichlorodiphenylcyclopropanes

IN Holan, George

PA Monsanto Chemicals Ltd., Australia

SO U.S., 5 pp. CODEN: USXXAM

DT Patent

LA English

GI

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI US 3962356	Α	19760608	US 1974-497776	19740815 <
US 3642910	A	19720215	US 1969-834177	19690617 <
US 3857956	A	19741231	US 1970-92235	19701123 <
PRAI AU 1963-36877	A	19631024		
US 1964-402949	A1	19641009		
US 1967-684554	A2	19671120		
US 1969-834177	A3	19690617		
US 1970-92235	A3	19701123		

$$R \xrightarrow{C1} R^1$$

AB The dichlorodiphenylcyclopropanes I (R = R1 = Et, EtO, Me, MeO, PrO; R, R1 = MeO, EtO), useful as insecticides, were prepared by insertion reaction of dichlorocarbene with 4-RC6H4C(C6H4R1-4):CH2.

L5 ANSWER 150 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN

Ι

AN 1976:420645 CAPLUS

DN 85:20645

TI 1-Cyclopropene-1-carboxylic acid esters from 1-chloro-1-cyclopropanecarboxylic acids

Sander, Volker; Weyerstahl, Peter

CS Inst. Org. Chem., Tech. Univ. Berlin, Berlin, Fed. Rep. Ger.

SO Angewandte Chemie (1976), 88(8), 259-60

CODEN: ANCEAD; ISSN: 0044-8249

DT Journal

ΑU

- AB Chlorocyclopropanecarboxylates I (R = R1 = Me, Ph) reacted with KOCMe3 in THF to give the cyclopropenecarboxylates II (71% for R = R1 = Ph).

 Treatment of I (R = R1 = H; R = H, R1 = Me) similarly gave polymers and III.
- L5 ANSWER 151 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
- AN 1976:134752 CAPLUS
- DN 84:134752
- TI Mass spectrometric investigation of 1,1-difluorocyclopropanes
- AU Kamel, M.; Kimpenhaus, W.; Riepe, W.
- CS Inst. Spektrochem. Angew. Spektrosk., Dortmund, Fed. Rep. Ger.
- SO Organic Mass Spectrometry (1976), 11(1), 79-85 CODEN: ORMSBG; ISSN: 0030-493X
- DT Journal
- LA German
- AB The mass spectra of 13 substituted 1,1-difluorocyclopropanes were obtained and fragmentation patterns determined Trends in fragmentation probabilities were correlated qual. with empirical substitution effects.
- L5 ANSWER 152 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
- AN 1976:120857 CAPLUS
- DN 84:120857
- TI Cyclopropanes. XXXVIII. Effect of 1-substituents on the stereochemical stability of the cyclopropyl radical
- AU Walborsky, H. M.; Collins, P. C.
- CS Dep. Chem., Florida State Univ., Tallahassee, FL, USA
- SO Journal of Organic Chemistry (1976), 41(6), 940-6 CODEN: JOCEAH; ISSN: 0022-3263
- DT Journal
- LA English
- AB The tert-butyl peresters of chiral 1-X-2,2-diphenylcyclopropanecarboxylic acids (X = F, Cl, OCH3) were prepared The peresters were decomposed in tetrahydrofuran at 100° to yield, inter alia, 1-X-2,2-diphenylcyclopropane. The stereochem, results showed that the effect of the 1-substituent in stabilizing the σ radical was in the order of F > OCH3 > Cl. This order follows what would be predicted by the Pauling-Walsh model based on the electronegativity of the substituent.
- L5 ANSWER 153 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
- AN 1975:478664 CAPLUS
- DN 83:78664
- TI Addition reactions to methylenecyclopropanes. IV. Convenient synthesis of 1,1-dihalospiropentanes
- AU Dunkelblum, E.; Singer, B.
- CS Dep. Org. Chem., Hebrew Univ., Jerusalem, Israel
- SO Synthesis (1975), (5), 323 CODEN: SYNTBF; ISSN: 0039-7881
- DT Journal
- LA English
- GI For diagram(s), see printed CA Issue.
- AB Methylenecyclopropanes I (R = H, Me, Ph) reacted with :CX2 (X = Cl,Br) from excess CHX3 and 50% NaOH in the presence of PhCH2NEt3+ Cl- and EtOH to give spiropentanes II in ≤95% yield.
- L5 ANSWER 154 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
- AN 1975:401876 CAPLUS

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DN 83:1876
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- TI Structure-activity relation of DDT analogs in crayfish giant axons
- AU Wu, Chau H.; Van den Bercken, Jozef; Narahashi, Toshio
- CS Med. Cent., Duke Univ., Durham, NC, USA
- SO Pesticide Biochemistry and Physiology (1975), 5(2), 142-9 CODEN: PCBPBS; ISSN: 0048-3575
- DT Journal
- LA English
- GI For diagram(s), see printed CA Issue.
- The effects of 14 DDT analogs (I analogs) on the resting and action potentials of the crayfish giant axon were investigated using the intracellular microelectrode technique. These analogs can be classified into 3 groups, excitatory, blocking, and dualist. An excitatory analog tends to increase the excitability of the axonal membrane, and has hydrophobic side chains on the para positions whose optimal size equals that of ethoxy group. A blocking analog suppresses the action potential without affecting the resting potential, and has hydrophilic side chains capable of forming hydrogen bonds. A dualist has both excitatory and blocking actions, and the latter may be related to restriction in rotation imposed by the grouping on the benzylic carbon. However, the dividing lines between these categories are not sharp, the compds. tending to fall along a spectrum between pure excitatory and pure blocking activity.
- L5 ANSWER 155 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
- AN 1975:154991 CAPLUS
- DN 82:154991
- TI Nuclear quadrupole resonance and stereochemistry. 4. Chlorocyclopropanes
- AU Delay, F.; Geoffroy, M.; Lucken, E. A. C.; Mueller, P.
- CS Dep. Org. Phys. Chem., Univ. Geneva, Geneva, Switz.
- SO Journal of the Chemical Society, Faraday Transactions 2: Molecular and Chemical Physics (1975), 71(3), 463-7
 CODEN: JCFTBS; ISSN: 0300-9238
- DT Journal
- LA English
- The 35Cl NQR frequencies of 22 chlorocyclopropanes showed that a 2-chloro substituent increased one of the 35Cl frequencies of the gem dichloro group by .apprx.0.8 MHz and the other by twice this amount; a further Cl at the 3-position, cis to the 2-Cl substituent, produced addnl. shifts of approx the same sizes. No analogous effect was observed for alkyl groups.
- L5 ANSWER 156 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
- AN 1975:139546 CAPLUS
- DN 82:139546
- TI Structures of 1,1-dichloro-2,2-diphenylcyclopropane and 1,1-dibromo-2,2-diphenylcyclopropane. Substitution effects on cyclopropane geometries
- AU Lauher, Joseph W.; Ibers, James A.
- CS Dep. Chem., Northwest. Univ., Evanston, IL, USA
- SO Journal of the American Chemical Society (1975), 97(3), 561-7 CODEN: JACSAT; ISSN: 0002-7863
- DT Journal
- LA English
- The structures of 1,1-dichloro- and 1,1-dibromo-2,2-diphenylcyclopropane were determined from 3-dimensional x-ray data collected by counter techniques. Both structures have unsym. cyclopropane rings with C-C bond lengths of 1.490 (3), 1.520 (3), and 1.529 (3) Å in the chloro compound and 1.477 (6), 1.508 (6), and 1.509 (6) Å in the bromo compound. In each structure the shortest C-C bond is that across the ring from the point of Ph substitution.
- L5 ANSWER 157 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
- AN 1975:43059 CAPLUS
- DN 82:43059
- TI Aryloxyaliphatic acids and their alkyl esters
- IN Phillips, Donal Kenney
- PA Sterling Drug Inc.
- SO Fr. Demande, 44 pp.
 - CODEN: FRXXBL
- DT Patent

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LA French
FAN.CNT 1
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PATENT NO.	KIND	DATE	APPLICATION NO.	DATE	
PI FR 2197586	A1	19740329	FR 1973-30434	19730822 <	
FR 2197586	B1	19770909			
PRAI US 1972-284537	Α	19720829			

GI For diagram(s), see printed CA Issue.

- AB Thirty-three phenoxyisobutyric acids [I; R = H, Et, Me; R1 = H, C1; R2, R3 = C1, Br, F (same or different); R4, R5 = H, Me (same or different); R6 = H, Me, Ph, Et; n = 0, 1] were prepared by different methods and showed effectiveness as anticholesteremics. The cycloaddn. of dihalocarbenes to ethers (II, R7 = alkyl), hydrolysis, and reaction with Me2CO-CHCl3 or BrCMe2CO2Et gave I. An-other preparation was the reaction of dihalocarbenes with (alkenylphenoxy)isobutyric acids (III). II were formed by the dehydration of 2,4-R1[R4CHR5C(OH)R6(CH2)n]C6H3OR7 and the Wittig reaction of 2,4-R1[R6CO(CH2)n]C6H3OR7 with (R4CHR5)P+Ph3 Br-.
- L5 ANSWER 158 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
- AN 1974:520744 CAPLUS
- DN 81:120744
- TI Carbenes. 7. Intramolecular reactions of vinyl- and allylphosphoryl carbenes
- AU Hartmann, A.; Welter, W.; Regitz, M.
- CS Fachber. Chem., Univ. Kaiserslautern, Kaiserslautern, Fed. Rep. Ger.
- SO Tetrahedron Letters (1974), (20), 1825-8 CODEN: TELEAY; ISSN: 0040-4039
- DT Journal
- LA German
- GI For diagram(s), see printed CA Issue.
- AB Irradiation of Me2C:CHC(:N2)P(O)(OMe)2 in C6H6 gave 33% cyclopropene I and 4% Me2C:C:CHP(O)(OMe)2. PhMeC:CHC-(:N2)P(O)(OMe)2 reacted similarly and also gave the indene derivative II. Irradiation of the diazobicyclohexenes III and IV, prepared by cycloaddn. of Ph2C:N2 with cyclopropenes I and V, resp., gave the bicyclobutanes VI and VII, resp.
- L5 ANSWER 159 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
- AN 1974:459297 CAPLUS
- DN 81:59297
- TI Mode of action of DDT analogs. Molecular orbital studies
- AU Holan, G.; Spurling, T. H.
- CS Div. Appl. Chem., CSIRO, Melbourne, Australia
- SO Experientia (1974), 30(5), 480-1 CODEN: EXPEAM; ISSN: 0014-4754
- DT Journal
- LA English
- AB A relation is given for correlating the insecticidal activity of DDT (I) [50-29-3] analogs with their electronic (mol. orbital) structure. When 5 DDT analogs were tested in a susceptible strain of housefly, insecticidal activity correlated well with the charge distribution of the mol. apex, as determined from mol. orbital calcns. at the CNDO / 2 level. The LD50 of the analogs decreased with the apex charge according to the equation: log LD50 = $\Delta\Sigma$ qs + C, where A is constant, qs is the charge on the insecticidal atoms, and C is a correlation coefficient equal to 0.998.
- L5 ANSWER 160 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
- AN 1974:133048 CAPLUS
- DN 80:133048
- TI 2-[(2,2-Dihalocyclopropyl)phenoxy]-2-methylpropionic acids and their esters
- IN Phillips, Donald Kenney
- PA Sterling Drug Inc.
- SO Ger. Offen., 46 pp.
 - CODEN: GWXXBX
- DT Patent
- LA German
- FAN.CNT 1

PATENT NO. KIND DATE APPLICATION NO. DATE

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	DK	141366	C	19800901				
	NO	143528	В	19801124	NO	1973-3388	19730828	<
	NO	143528	C	19810304				
	FI	58629	В	19801128	FI	1973-2675	19730828	<
	FI	58629	С	19810310				
	SE	417828	В	19810413	SE	1973-11687	19730828	<
	SE	417828	С	19810730				
	NL	7311903	A	19740304	NL	1973-11903	19730829	<
	NL	180004	В	19860716				
	NL	180004	C	19861216				
	JΡ	49056958	A2	19740603	JР	1973-96261	19730829	<
	JP	58005175	B4	19830129				
	US	3948973	Α	19760406	US	1974-443418	19740219	<
	ΑT	7504817	A	19760115	AT	1975-4817	19750623	<
	ΑT	332372	В	19760927				
	ΑT	7504818	A	19760115	AT	1975-4818	19750623	<
	ΑT	332373	В	19760927				
	JР	58074636	A2	19830506	JP	1982-94645	19820602	<
	JP	60000335	B4	19850107				
	JP	58083649	A2	19830519	JP	1982-94644	19820602	<
	JP	60000334	B4	19850107				
PRAI	US	1972-284577	A	19720829				
	GB	1973-38311	Α	19730813				
	AT	1973-7447	Α	19730827				
	CH	1973-12272	Α	19730827				
~ -				1 C3 T				

GI For diagram(s), see printed CA Issue.

AB About 25 cyclopropyl derivs. (I, x = 2, 3, or 4; n = 0 or 1; Rm = H, 1-Me, 1-Et, 1- or 3-Ph, 1,3-Me2, or 3,3-Me2; R1,R2 = Br, Cl, or F; R3 = H or 3-Cl (in the case of x = 4); R4 = H, Me, or Et; and II) were prepared and useful as anticholesteremics and hypotriglyceridemics in the treatment of arteriosclerosis. Thus, the phenol III (x = 4, n = 0, Rm = 1-Me, R1 = R2 = Cl, R3 = H), CHCl3, and Me2CO were refluxed in the presence of NaOH to give the corresponding acid I (R4 = H). Ph3P+Et Br- was treated successively with NaH in Me2SO and with 4-MeCOC6H4OCMe2CO2Me to give 4-MeCH:CMeC6H4OCMe2CO2Me (IV). IV was treated with CHCl3 in pentane in the presence of Me3COK to give I (x = 4, n = 0, Rm - 1,3-Me2, R2 = R2 = Cl, R3 = H, R4 = Me), which on alkaline hydrolysis gave the corresponding acid.

- L5 ANSWER 161 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
- AN 1974:120354 CAPLUS
- DN 80:120354
- TI Synthesis and ring cleavage of geminal chlorofluoro- and difluorocyclopropanes
- AU Weyerstahl, Peter; Schwartzkopff, Udo; Nerdel, Friedrich
- CS Inst. Org. Chem., Tech. Univ., Berlin, Fed. Rep. Ger.
- SO Justus Liebigs Annalen der Chemie (1973), (12), 2100-10 CODEN: JLACBF; ISSN: 0075-4617
- DT Journal
- LA German
- GI For diagram(s), see printed CA Issue.
- AB Reaction of Me2C:CRR1 (R = Me, Et, or CH:CMe2; R1 = H or Me) with CHClF2 or CHCl2F and ethylene oxide and Et4NBr gave the dihalocyclopropanes I (X, Z = Cl or F) and II (X, Z = Cl or F), CH2:CMeCF:CRR1, ClCH2CH2OCMe2CF:CRR1, and Me2C:CFCRR1OCH2CH2Cl. Ring cleavage of the initially formed dihalocyclopropanes depends largely on the stability of the intermediate allyl cation.

- L5 ANSWER 162 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
- AN 1974:108027 CAPLUS
- DN 80:108027
- TI Stable 1,1-diiodo- and 1-chloro-1-iodocyclopropane
- AU Mathias, Rolf; Weyerstahl, Peter
- CS Inst. Org. Chem., Tech. Univ. Berlin, Berlin, Fed. Rep. Ger.
- SO Angewandte Chemie (1974), 86(1), 42-3 CODEN: ANCEAD; ISSN: 0044-8249
- DT Journal
- LA German
- GI For diagram(s), see printed CA Issue.
- The halocyclopropanes [I; R = Et, Me3C, Ph, 4-ClC6H4; R1 = H, Me; R2 = H, Ph; R3 = H; or RR3 = (CH2)4; X = Cl, iodo] were prepared, partly as isomeric mixts., by adding NaOH to RR1C:CR2R3 and XCHI2 in CH2Cl2-Et3N+CH2Ph Cl-and heating the mixts. for 3 hr at 50°. The aromatic substituted I (X = iodo) were more stable and obtained in higher yields than the aliphatic substituted I (X = iodo). I (X = Cl) were more stable and obtained in higher yields than I (X = iodo).
- L5 ANSWER 163 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
- AN 1974:107864 CAPLUS
- DN 80:107864
- TI Molecular polarizability. Conformational study of substituted arylcyclopropanes
- AU Aroney, Manuel J.; Calderbank, Kingsley E.; Stootman, Heather J.
- CS Sch. Chem., Univ. Syd., Sydney, Australia
- SO Journal of the Chemical Society, Perkin Transactions 2: Physical Organic Chemistry (1972-1999) (1973), (15), 2060-3
 CODEN: JCPKBH; ISSN: 0300-9580
- DT Journal
- LA English
- AB The dipole moments and molar Kerr consts. of 11 aryl-gemdihalocyclopropanes were analyzed to deduce preferred solution state conformations.
- L5 ANSWER 164 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
- AN 1973:545603 CAPLUS
- DN 79:145603
- TI Reactivity of unsaturated organophosphorus compounds in the 1,3-dipolar cycloaddition of diaryldiazomethanes
- AU Pudovik, A. N.; Gareev, R. D.; Stabrovskaya, L. A.; Evstaf'ev, G. I.; Remizov, A. B.
- CS Kazan. Gos. Univ. im. Ul'yanova-Lenina, Kazan, USSR
- SO Zhurnal Obshchei Khimii (1973), 43(8), 1674-82 CODEN: ZOKHA4; ISSN: 0044-460X
- DT Journal
- LA Russian
- AB Kinetic data on the 1,3-dipolar addition of Ph2CN2 to R2P(X)CR1:CH2 [R2 = (MeO)2, (EtO)2, (PrO)2, (C1CH2CH2O)2, (PhO)2, (p-BrC6H4O)2, (p-MeC6H4O)2, (m-MeC6H4O)2, Et2, EtPh, Ph2, OCH2CH2CH2O, (Me2N)2; R1 = H, Me; X = O, S] were determined in polar and nonpolar solvents. The reaction was 1st order in respect to Ph2CN2 and 2nd order overall. The mechanism was a 1-step polycentric type with cyclic electron transfer; the effect of substituents on the rate was correlated with shifts in the NMR and ir spectra of the P compds. The initial products were Δ1-pyrazolines which, depending on the conditions used, either decomposed to cyclopropane derivs. by loss of N2 or isomerized to Δ2-pyrazolines. The effect of solvent polarity on kinetics of the reaction favored a cyclic transition state in which the terminal C atom of the vinyl group was neg. charged while the central C atom of the diazocompd. was neg. charged, i.e., Ph2CN2 acted as an electrophile. Activation energy was 12.5 kcal/mole at 60°; ΔS was -35.2 entropy units.
- L5 ANSWER 165 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
- AN 1973:418790 CAPLUS
- DN 79:18790
- TI Cyclopropanes. XXXIII. Reaction of lithium metal surfaces with optically active 1-halo-1-methyl-2,2-diphenylcyclopropane

- AU Walborsky, H. M.; Aronoff, M. S.
- CS Dep. Chem., Florida State Univ., Tallahassee, FL, USA
- SO Journal of Organometallic Chemistry (1973), 51, 55-75 CODEN: JORCAI; ISSN: 0022-328X
- DT Journal
- LA English
- The reaction of Li metal surfaces with optically active 1-halo-1-methyl-2,2-diphenylcyclopropane gave the corresponding Li derivative which is partially racemized. The amount of racemization observed is a function of the halide (I > Br > Cl), the Na content of the Li metal as well as its particle size.
- L5 ANSWER 166 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
- AN 1973:405070 CAPLUS
- DN 79:5070
- TI Reaction of 0,0'-diethyl α -lithiomethyl phosphonate with organic dihalides
- AU Oshima, Koichiro; Shirafuji, Tamio; Yamamoto, Hisashi; Nozaki, Hitosi
- CS Dep. Ind. Chem., Kyoto Univ., Kyoto, Japan
- SO Bulletin of the Chemical Society of Japan (1973), 46(4), 1233-5 CODEN: BCSJA8; ISSN: 0009-2673
- DT Journal
- LA English
- GI For diagram(s), see printed CA Issue.
- Dibromocyclopropanes I [R = H, R1 = Ph or cyclohexyl; RR1 = (CH2)n, n = 4, 6, 10; or RR1 = CH2CH:CHCH2] were reduced to the monobromo derivs. (65-82% yield) by treatment with (EtO)2P(O)CH2Li (II) at -78° in THF; 1,1-dibromo-2,2-diphenylcyclopropane gave 62% 1,1-diphenylcyclopropane with >6 equivalent II. Dehalogenation of PhCH2Cl and Ph2CHCl gave PhCH2CH2Ph and Ph2CHCHPh2, resp. in the presence of II; PhCH:CHCH2Cl and trans-PhCH:CHBr underwent deprotonation to PhCH:CH-CH2CHClCH:CHPh and PhCH:CHC.tplbond.CPh, resp.
- L5 ANSWER 167 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
- AN 1973:159807 CAPLUS
- DN 78:159807
- TI Synthesis and mass spectral behavior of representative 1,1-dichloro-2-phenylcyclopropanes and 1,1-dichloro-2-ferrocenylcyclopropanes
- AU Gokel, George W.; Shepherd, James Peter; Weber, William P.; Boettger, Heinz G.; Holwick, Jann L.; McAdoo, David
- CS Dep. Chem., Univ. South. California, Los Angeles, CA, USA
- SO Journal of Organic Chemistry (1973), 38(10), 1913-8 CODEN: JOCEAH; ISSN: 0022-3263
- DT Journal
- LA English
- AB Addnl. data considered in abstracting and indexing are available from a source cited in the original document. 1,1-Dichloro-2-ferrocenylcyclopropanes were prepared in good yield by addition of dichlorocarbene to vinylferrocenes under phase transfer catalysis conditions. The mass spectral fragmentation pattern of 1,1-dichloro-2-phenylcyclopropanes and of 1,1-dichloro-2-ferrocenylcyclopropanes are similar.
- L5 ANSWER 168 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
- AN 1973:158769 CAPLUS
- DN 78:158769
- TI Cyclopropanes. XXXII. Mechanism of Grignard formation
- AU Walborsky, H. M.; Aronoff, M. S.
- CS Dep. Chem., Florida State Univ., Tallahassee, FL, USA
- SO Journal of Organometallic Chemistry (1973), 51, 31-53 CODEN: JORCAI; ISSN: 0022-328X
- DT Journal
- LA English
- AB The radical nature of the Grignard formation reaction is discussed based on product anal. from the reaction of 1-halo 1-methyl-2,2-diphenylcyclopropane with Mg metal in Et20-d10 and THF-d8; the radical intermediates formed largely disproportionate on the surface of the Mg and not in solution The stereochem. is consistent with a surface-radical

mechanism. Neither the particle size nor the purity of the Mg effect the stereochem. of the reaction.

- ANSWER 169 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN 1973:130294 CAPLUS AN DN 78:130294 NQR of chlorine in chlorocyclopropanes and effect of conjugation TΤ ΑU Murin, A. N.; Murin, I. V.; Kazakov, V. P.; Sivkov, V. P. CS Leningr. Gos. Univ., Leningrad, USSR Zhurnal Strukturnoi Khimii (1973), 14(1), 158-61 SO CODEN: ZSTKAI; ISSN: 0136-7463 DT Journal LA Russian The effect of the conjugation of the C-Cl bond in dichlorcyclopropanes was AΒ studied by NQR of 35Cl in pure chlorocyclopropane, 2,2-dichloro-1-methycyclopropane, 7,7-dichloronorcarane, 1,1-dichrocyclo-propane, 2,2-dichloro-1-benzylcyclopropane, 2,2-dichloro-1,1-dimethylcyclopropane, 2,2-dichloro-1-phenylcyclopropane, 2,2-dichloro-1-ethyl-1-phenylpropane, 7,7-dichloro-2-phenylnorcarane, 2,2,2',2'-tetrachlorobicyclopropane, 2,2-dichloro-1,1-diphenylcyclopropane, and pentachlorocyclopropane at 77°K. The higher values of the 35Cl frequencies in the chlorocyclopropanes than in the linear analogs were due to a higher electronegativity of the ring C with respect to Cl than the electronegativity of this C with respect to other C atoms. The NOR method was not convenient for the study of the conjugation effect of the cyclopropane ring with substituents having π -electrons. ANSWER 170 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN 1973:124706 CAPLUS AN DN 78:124706 Preparation of 1-methyl-2,2-diphenylcyclopropylcobaloxime and theoretical TT considerations for its mode of formation Jensen, Frederick R.; Buchanan, David H. CS Dep. Chem., Univ. Calif., Berkeley, CA, USA Journal of the Chemical Society, Chemical Communications (1973), SO CODEN: JCCCAT; ISSN: 0022-4936 DT Journal LA English Reaction of pyridine [bis(di-methylglyoximato)]cobalt(I) with 1-AB methyl-2,2-diphenylcyclopropyl bromide gave 60% 1-methyl-2,2diphenycyclopropyl-(pyridine)cobaloxime. Five possible mechanisms for the reaction of low-valent metal ions with alkyl halides were proposed. ANSWER 171 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN ΑN 1973:72307 CAPLUS 78:72307 DN Cycloaddition of diphenyldiazomethane to allenyl phosphonates ΤI Pudovik, A. N.; Khusainova, N. G.; Timoshina, T. V. AU Kazan. Gos. Univ., Kazan, USSR CS Zhurnal Obshchei Khimii (1972), 42(10), 2159-62 SO CODEN: ZOKHA4; ISSN: 0044-460X DT Journal LΑ GI For diagram(s), see printed CA Issue. AB (EtO) 2P(O) CH: CCH was treated with Ph2CN2 at room temperature to give 37% I; at 75°, 69% II is formed. At room temperature after 20 days (EtO) 2P(O) CPh:C:CH2 gave 36% 3-(diethoxyphosphinyl)-2,2,3-triphenyl-1methylenecyclopropane, also formed at 75° by loss of N. L5 ANSWER 172 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN AN1973:57816 CAPLUS DN78:57816 Reduction of alkyl-, aryl-, and vinyl-gem-dihalocyclopropanes into ΤI
- corresponding cyclopropane hydrocarbons
- AU Nefedov, O. M.; Shafran, R. N.; Novitskaya, N. N. CS Inst. Org. Khim. im. Zelinskogo, Kazan, USSR
- SO Zhurnal Organicheskoi Khimii (1972), 8(10), 2075-9 CODEN: ZORKAE; ISSN: 0514-7492

- DT Journal
- LA Russian
- AB Fourteen title gem-dichloro- and -dibromocyclopropanes and 8 gem-dichloroand dibromonorcaranes were reduced to the corresponding hydrocarbons in ≤95% yield by 1-1.2 equivalent of 4-7% Na in liquid NH3; no hydrogenolysis products were observed
- L5 ANSWER 173 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
- AN 1973:54048 CAPLUS
- DN 78:54048
- TI Compositions for combating insects of the genus Heliothis
- IN Ludvik, George F.; Darlington, Walter A.
- PA Monsanto Co.
- SO U.S., 4 pp.
 - CODEN: USXXAM
- DT Patent
- LA English
- FAN.CNT 1

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI US 3692915	Α	19720919	US 1970-37026	19700513 <
PRAI US 1970-37026	A	19700513		

AB Heliothis zea was controlled by a mixture of 1,1-dichloro-2,2-bis(4'-chlorophenyl)cyclopropane (I) [3575-15-3] and polychlorocamphene. Thus, as shown in caging expts., spraying of cotton with a mixture of 0.05 lb I and 0.125 lb polychlorocamphene/acre induced a 70% mortality of H. zea larvae.

- L5 ANSWER 174 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
- AN 1973:3850 CAPLUS
- DN 78:3850
- TI Insecticides. I. Crystal structures of 1,1-bis(p-chlorophenyl)-2,2-dichlorocyclopropane and 1,1-bis(p-ethoxyphenyl)-2,2-dimethylpropane
- AU DeLacy, T. P.; Kennard, C. H. L.
- CS Dep. Chem., Univ. Queensl., Brisbane, Australia
- SO Journal of the Chemical Society, Perkin Transactions 2: Physical Organic Chemistry (1972-1999) (1972), (14), 2141-7 CODEN: JCPKBH; ISSN: 0300-9580
- DT Journal
- LA English
- Crystal and mol. structures were determined by x-ray anal. of 1.1-bis(p-chlorophenyl)-2,2-dichlorocyclopropane (I) and 1.1-bis(p-ethoxyphenyl)-2,2-dimethylpropane (II); the structures of I and II were refined to R 0.061 and 0.035 for 2019 and 947 observed independent reflections, resp. Crystals of I were monoclinic, space group P21/a, with a 1735.1, b 1570.1, c 1111.1 pm, β 97.09, and Z = 8; crystals of II were orthorhombic, space group Pca21, with a 2291.2, b 1042.4, c 780.9 pm, and Z = 4. I adopted a butterfly configuration; there was considerable interaction between the cyclopropane and aromatic rings. The structure of II is similar to that of I except that the ethoxy groups lie coplanar to the attached benzene rings and in a nonsym. trans-configuration.
- L5 ANSWER 175 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
- AN 1973:3541 CAPLUS
- DN 78:3541
- TI Anisotropy of polarizability and spatial structure of phenylcyclopropanes and their analogs
- AU Arbuzov, B. A.; Vereshchagin, A. N.; Vul'fson, S. G.; Monetina, L. A.
- CS Inst. Org. Fiz. Khim. im. Arbuzova, Kazan, USSR
- SO Doklady Akademii Nauk SSSR (1972), 205(5), 1096-9 CODEN: DANKAS; ISSN: 0002-3264
- DT Journal
- LA Russian
- GI For diagram(s), see printed CA Issue.
- AB The conformations of phenylcyclopropanes (I; R = H, Me, Ph; R1 = H, Cl, Br) were examined in light of existing dipole moment information and their polarizabilities. The conformational analysis revealed that 1-substituted members in which cis-vicinal effect is not pronounced have as the most stable conformation that with the rotational angle of the Ph group Φ =

- 90°. For the 1,1-diphenylcyclopropane and its 2-halo analogs the angle presented by the ring planes may be 30° or 38°; in 2,2-dihalo analogs in which the ortho H interference is possible, the rotational angle is close to 90°.
- L5 ANSWER 176 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
- AN 1972:513391 CAPLUS
- DN 77:113391
- TI Solvolysis of cyclopropyl halides. II. 2-Phenylcyclopropyl bromides
- AU Hausser, Jack W.; Grubber, Michael J.
- CS Dep. Chem., Duquesne Univ., Pittsburgh, PA, USA
- SO Journal of Organic Chemistry (1972), 37(17), 2648-50 CODEN: JOCEAH; ISSN: 0022-3263
- DT Journal
- LA English
- AB 2,2-Diphenylcyclopropyl bromide and cis- and trans-2-phenylcyclopropyl bromide were prepared and solvolyzed in HOAc to give the corresponding ring opened allylic acetate. First order rate consts. and activation parameters were determined The reaction is considered in terms of the effect of the leaving group on the ring opening process.
- L5 ANSWER 177 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
- AN 1972:495076 CAPLUS
- DN 77:95076
- TI NQR analysis of the nature of the carbon-chlorine bond in chlorocyclopropanes
- AU Murin, A. N.; Murin, I. V.; Kazakov, V. P.; Sivkov, V. P.
- CS Leningr. Gos. Univ., Leningrad, USSR
- SO Zhurnal Strukturnoi Khimii (1972), 13(3), 531-4 CODEN: ZSTKAI; ISSN: 0136-7463
- DT Journal
- LA Russian
- AB The 35Cl NQR spectra of 12 substituted chlorocyclopropanes were analyzed.

 The degree of ionic character of the C-Cl bond and effective orbital electronegativity of the C atom bonded to Cl were calculated assuming 21% s-hybridization of Cl.
- L5 ANSWER 178 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
- AN 1972:415570 CAPLUS
- DN 77:15570
- TI Selected toxicants for control of lice on poultry at Kerrville, Texas, 1961-69
- AU Hoffman, R. A.; Hogan, B. F.
- CS Entomol. Res. Div., Agric. Res. Serv., Kerrville, TX, USA
- SO Journal of Economic Entomology (1972), 65(2), 468-70 CODEN: JEENAI; ISSN: 0022-0493
- DT Journal
- LA English
- Out of 65 insecticides tested by a new technique for the control of poultry lice (mixed species, principally Menacanthus stramimeus), 15 gave control equal or superior to that of malathion [121-75-5]. Crotoxyphos [7700-17-6], Zectran (I) [315-18-4], and Hooker HRS-1422 (3,5-diisopropylphenyl N-methylcarbamate) [330-64-3] gave the best results.
- L5 ANSWER 179 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
- AN 1972:122911 CAPLUS
- DN 76:122911
- TI Candidate chlorinated hydrocarbon chemical for resistant Aedes nigromaculis control
- AU Kingsford, Elmer; Hazeltine, William
- CS Butte Cty. Mosquito Abatement Dist., Oroville, CA, USA
- Proceedings and Papers of the Annual Conference of the California Mosquito Control Association (1971), 39, 112-13
 CODEN: PCCMAN; ISSN: 0091-6501
- DT Journal
- LA English
- AB Monsanto 0412 (1,1-bis(p-chlorophenyl)-2,2-dichlorocyclopropane (I) [3575-15-3] which differed from DDT (II) [50-29-3] at the center of

the mol. where a 3-C ring with 2 Cl atoms was substituted for a 2-C chain with 3 Cl atoms, was approx. 10-fold more active than II against II-resistant A. nigromaculis. On A. vexans I was equal in toxicity to II, but less active than parathion [56-38-2] or Baytex [55-38-9]. On Culex pipiens from a laboratory colony, I was twice as active as II and approx. one-fifth as active as parathion.

- L5 ANSWER 180 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
- AN 1972:85154 CAPLUS
- DN 76:85154
- TI Transannular neophyl rearrangement
- AU Wilt, James W.; Dabek, Rose A.; Welzel, Kippert C.
- CS Dep. Chem., Loyola Univ., Chicago, IL, USA
- SO Journal of Organic Chemistry (1972), 37(3), 425-30
 - CODEN: JOCEAH; ISSN: 0022-3263
- DT Journal
- LA English
- AB The radical rearrangement in solution of a phenyl group across a cyclohexane ring via bicyclo[2.2.1]heptyl and bicyclo-[2.2.2]octyl species was achieved. This transannular rearrangement did not occur in analogs via smaller sized bicyclic species. In these cases the parent structures were retained or ring-opening occurred.
- L5 ANSWER 181 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
- AN 1971:551271 CAPLUS
- DN 75:151271
- TI Stereochemistry of tris(triphenylphosphine)rhodium chloride decarbonylation of aldehydes
- AU Walborsky, H. M.; Allen, L. E.
- CS Dep. Chem., Florida State Univ., Tallahassee, FL, USA
- SO Journal of the American Chemical Society (1971), 93(21), 5465-8 CODEN: JACSAT; ISSN: 0002-7863
- DT Journal
- LA English
- AB A series of aldehydes differing in the hybridization of the carbon atom to which the carbonyl group is attached, i.e., (-)(R)-2-methyl-2-phenylbutanal, (+)(R)-1-methyl-2,2-diphenylcyclopropanecarboxaldehyde, and (E)-α-ethylcinnamaldehyde, was decarbonylated using tris(triphenylphosphine)rhodium chloride. The products, (+)(S)-2-phenylbutane, (+)(S)-1-methyl-2,2-diphenylcyclopropane, and (Z)-1-phenyl-1-butene, were formed with 81, 94, and 100% retention of optical activity, resp. The optical purity in the decarbonylation of a series of 1-substituted cyclopropyl aldehydes varied from 83 to 6%. A cleavage radical pair disproportionation mechanism is proposed for the reaction on the basis of the stereochem. results. The decarbonylation of 1-methyl-2,2-diphenylcyclopropanecarboxaldehyde-d was used to demonstrate the intramol. reaction as well as illustrate its application to the synthesis of specifically D-labeled compds.
- L5 ANSWER 182 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
- AN 1971:540046 CAPLUS
- DN 75:140046
- TI Cyclopropanes. XXX. Haller-Bauer cleavage of phenyl cyclopropyl ketones
- AU Walborsky, Harry M.; Allen, Lewis E.; Traenckner, H. J.; Powers, E. J.
- CS Dep. Chem., Florida State Univ., Tallahassee, FL, USA
- SO Journal of Organic Chemistry (1971), 36(20), 2937-41 CODEN: JOCEAH; ISSN: 0022-3263
- DT Journal
- LA English
- AB Syntheses and establishment of the ab. configurations of 1-chloro, 1-fluoro, and 1-methoxy-2,2-diphenylcyclopropyl phenyl ketones are described. The optically active ketones were cleaved with NaNH2 to yield optically active 1-chloro, 1-fluoro, and 1-methoxy-2,2-diphenylcyclopropane, resp.
- L5 ANSWER 183 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
- AN 1971:529714 CAPLUS
- DN 75:129714
- TI Reaction of ethyl α -fluoroacrylate with aliphatic diazo compounds

- AU Kotikyan, Yu. A.; Petrovskii, P. V.; Dyatkin, B. L.; Knunyants, I. L.
- CS USSR
- SO Zhurnal Organicheskoi Khimii (1971), 7(7), 1363-7 CODEN: ZORKAE; ISSN: 0514-7492
- DT Journal
- LA Russian
- The reaction of H2C:CFCO2Et (I) with CH2N2 gave unstable Et 3-fluoro-1-pyrazoline-3-carboxylic acid ester which at room temperature decomposes to Et pyrazole-3-carboxylic acid ester. The reaction of I with N2CHCO2Et (II) gave only 1 F-containing compound: FCH2CO2Et (resulting from the reaction of II with HF) and di-Et pyrazole-3,5-dicarboxylic acid ester. The reaction of I with II in the presence of Cu powder gave mostly polymers, Et fumarate, Et maleate, and small amount of di-Et 1-fluorocyclopropane-1,2-dicarboxylic acid ester (formed by loss of N and ring contraction of the corresponding pyrazole diester). Similarly, I reacts with 9-diazofluorene to give 2-fluoro-2-ethylcarboxyspiro[cyclopropane-1,9'-fluorene] and N.
- L5 ANSWER 184 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
- AN 1971:517886 CAPLUS
- DN 75:117886
- TI Conformational effects in compounds with six-membered rings. VIII Preferred orientations of alkyl groups in allenes and in 2-alkyl-1,3-dioxanes and -dioxolanes
- AU Riddell, F. G.; Robinson, M. J. T.
- CS Robert Robinson Lab., Univ. Liverpool, Liverpool, UK
- SO Tetrahedron (1971), 27(17), 4163-9 CODEN: TETRAB; ISSN: 0040-4020
- DT Journal
- LA English
- AB The preferred orientations of ethyl and isopropyl groups in 1-alkyl-1-3,3-diphenylallenes and in 2-alkyl-1,3-dioxanes and -dioxolanes were determined from the temperature dependence of the spin-spin coupling consts. for appropriate vicinal protons. In the allenes, a Me group rather than a H atom eclipses a double bond but in the cyclic acetals skew interactions between Me groups and O atoms are minimized in the preferred conformations. The conformational preferences in simple ketones and aldehydes depend primarily on the double bonds rather than on the electronegativity of the O atom of the CO-group.
- L5 ANSWER 185 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
- AN 1971:488692 CAPLUS
- DN 75:88692
- TI Reaction of diphenyldiazomethane with tertiary vinyl- and allylphosphine oxides
- AU Pudovik, A. N.; Gareev, R. D.; Aganov, A. V.; Raevskaya, O. E.; Stabrovskaya, L. A.
- CS Kazan. Gos. Univ., Kazan, USSR
- SO Zhurnal Obshchei Khimii (1971), 41(5), 1008-16 CODEN: ZOKHA4; ISSN: 0044-460X
- DT Journal
- LA Russian

L5

- GI For diagram(s), see printed CA Issue.
- AB Ph2CN2 and Et2P(0)CH:CH2 in hot C6H6 gave 97% N, and, after treatment with EtOH, some of the oxide was recovered along with 92.5% I (R = R1 = Et) (Ia). Similarly were prepared I (R = Et, R1 = Ph) and I (R1 = R2 = Ph). Reaction of 1.4 g Et2P(O)CH.CH2 with 3 g Ph2CN2 in Et2O-hexane 1 hr at 30° gave 84% II (R = R1 = Et) (IIa). Similarly prepared II were (R and R1 given): Bu, Bu; Et, Ph; and Ph, Ph. These with Et3N in C6H6 kept 1 hr isomerized to 90-7% III (R and R1 given): Et, Et; Bu, Bu; Et, Ph; and Ph, Ph. The isomerization was also carried out with KOH in absolute EtOH, dry HCl in EtOH, or contact with MeCN at room temperature Pyrolysis of IIa in refluxing C6H6 1 hr gave 98% N and 96% Ia. EtMgBr and I (R = R1 = Cl) gave 37% Ia. Et2P(O)CH2CH:CH2 and Ph2CN2 at 120° gave 56% N and after treatment with EtOH gave benzophenone azine, Ph2CO, Ph4C2H2, and 5% I (R = R1 = Ph).Ir spectra of the Δ2-pyrazolines indicated their tendency to associate by H bonding.

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AN
     1971:141084 CAPLUS
DN
     74:141084
     Reactions of olefins with dihalocarbenes
TI
     Dehmlow, Eckehard V.; Schoenefeld, Joachim
ΑU
     Org.-Chem. Inst., Tech. Univ. Berlin, Berlin, Fed. Rep. Ger.
CS
     Justus Liebigs Annalen der Chemie (1971), 744, 42-50
SO
     CODEN: JLACBF; ISSN: 0075-4617
DT
     Journal
LA
     German
     For diagram(s), see printed CA Issue.
GI
     Dichlorocyclopropanes were prepared by reaction of dichlorocarbene generated
AB
     from CHCl3, NaOH, and catalytic PhCH2NEt3Cl with olefins, e.g.
     trans-PhCH:CHPh, Ph2C:CH2, PhCH:CH2, or PhCH:CHCH:CHPh. Similarly
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- cyclooctatetraene gave 24% 9,9-dichlorobicyclo[6.1.0]nona-2,4,6-triene and 16% bisadduct 5,5,10,10-tetrachlorotricyclo-[7.1.0.04,6]deca-2,7-diene
 - (I). Acetylenes gave only low yields of cyclopropenones. Dibromocarbene reacted similarly but with low yields.
- ANSWER 187 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN L5 AN 1971:111747 CAPLUS

DN 74:111747

TI 1,1-bis(p-nitrophenyl)-2,2-dihalocyclopropane insecticides

IN Holan, George

- PA Monsanto Chemicals (Australia) Ltd.
- SO U.S., 4 pp. Division of U.S. 3,481,993 CODEN: USXXAM
- DT Patent
- LΆ English

FAN.CNT 1

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI US 3551577	Α	19701229	US 1969-810071	19690130 <
PRAI US 1969-810071	Α	19690130		

PR

- Division of U.S. 3,481,993. (CA 72: 66594q). The disclosure is the same, AB but the claims are different.
- ANSWER 188 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN L5
- AN1971:75917 CAPLUS
- DN 74:75917
- Cyclopropanes. XXIX. Stereochemistry of the 1-methyl-2,2-ΤI diphenylcyclopropyl radical in and out of solvent cage
- ΑU Walborsky, Harry M.; Chen, Jong-Chen
- CS Dep. Chem., Florida State Univ., Tallahassee, FL, USA
- SO Journal of the American Chemical Society (1971), 93(3), 671-5 CODEN: JACSAT; ISSN: 0002-7863
- DT Journal
- LA English
- The 1-methyl-2,2-diphenylcyclopropyl radical (I) was generated in solution AB from from a variety of optically active precursors to yield cyclopropyl derivs. which were largely if not entirely racemized. However, when I disproportionates within the solvent cage, 1-methyl-2,2-diphenylcyclopropane obtained was 31-37% optically pure (66-68% retention of configuration). The disproportionation occurred within a solvent cage.
- L5 ANSWER 189 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
- 1971:52932 CAPLUS AN
- DN 74:52932
- Net retention in the reduction of optically active cyclopropyl bromides by ΤI di-n-butyltin dihydride. Cage reduction of a rapidly inverting cyclopropyl radical
- Altman, Lawrence J.; Erdman, Timothy R. ΑU
- Dep. Chem., Stanford Univ., Stanford, CA, USA CS
- SO Tetrahedron Letters (1970), (56), 4891-4 CODEN: TELEAY; ISSN: 0040-4039
- Journal DΤ
- LA English
- AB Cyclopropyl bromides (I) and (II) are treated with Bu2SnH2 to give III and IV in a front side cage reduction Free radicals are involved in the reactions, and hexane, hexadecane, and paraffin oil are used as solvents.

Inversion and rotation are faster than reduction at high viscosities.

- L5 ANSWER 190 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
- AN 1971:31578 CAPLUS
- DN 74:31578
- TI Competitive bicyclobutane and allene formation from phenyl-substituted gem-dibromocyclopropanes
- AU Moore, William Robert; Hill, John Benjamin
- CS Dep. Chem., Massachusetts Inst. Technol., Cambridge, MA, USA
- SO Tetrahedron Letters (1970), (52), 4553-6 CODEN: TELEAY; ISSN: 0040-4039
- DT Journal
- LA English
- GI For diagram(s), see printed CA Issue.
- AB Allenes, R3R2C:C:CR1R (I) and bicyclobutanes (II) are prepared by the reaction of III with MeLi. II are obtained only from III (R3 = Me) compds. III (R2 = R3 = Me) give mixts. of I and II. The allene is the only product obtained from III (R = H, R1 = Me, R2 = R3 = Ph).
- L5 ANSWER 191 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
- AN 1970:531061 CAPLUS
- DN 73:131061
- TI Synthesis and metallation of (+)-(R) and (-)-(S)-1-fluoro-1-methyl-2,2-diphenylcyclopropane
- AU Powers, Edward J.
- CS Florida State Univ., Tallahassee, FL, USA
- SO (1969) 118 pp. Avail.: 70-6301 From: Diss. Abstr. Int. 1970, 30(10), 4568-9
- DT Dissertation
- LA English
- AB Unavailable
- L5 ANSWER 192 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
- AN 1970:477340 CAPLUS
- DN 73:77340
- TI Reactions of diphenyldiazomethane with derivatives of isopropenylphosphonic acid
- AU Pudovik, A. N.; Gareev, R. D.
- CS Kazan. Gos. Univ. im. Ul'yanova-Lenina, Kazan, USSR
- SO Zhurnal Obshchei Khimii (1970), 40(5), 1025-30 CODEN: ZOKHA4; ISSN: 0044-460X
- DT Journal
- LA Russian
- GI For diagram(s), see printed CA Issue.
- AB Adding 4.25 g Ph2CN2 at 75° to 7.8 g (EtO)2P(O)CMe:CH2 over 5 hr gave 94% N, and the residue, treated with EtOH, yielded some unreacted ester and a fraction, b1 162-79°, which with KMnO4 gave 75% I (R = Et), b0.002 158-9°. Similarly were prepared the following analogs: $R = Me, 70\%, m. 71^{\circ}, and R = Ph, 90.5\%, m. 104-6^{\circ}.$ The reaction as above but in the presence of a catalytic amount CuSO4 gave 73% N, while the residue treated with EtOH yielded 46% benzophenonazine, m. 162°, some unreacted ester, and 7.5% BzPh, as well as 3.7% I (R = Et). Ph2C:CH2 (23 g) at 150-70° mixed with 1.7 g (MeO)2P(O)CMeN2 gave 82% N and 46.5% I (R = Me). CH2:CMePOCl2 (10.5 g) and 6.4 g Ph2CN2 mixed over 1.5 hr and held at 45° gave 96% N, some starting material, and a fraction, b0.01 156-7°, which with KMnO4 gave 79% phosphonic dichloride analog of I, b0.005 151-2°, n20D 1.5934. This and PhOH with pyridine gave 41.9% I (R = Ph), identical with the above. (PhO)2P(O)CMe:CH2 and Ph2CN2 in petroleum ether 3 days gave 3-diphenoxyphosphono-3-methyl-5,5-diphenyl-1-pyrazoline, m. 107-8°, which heated to 75° gave N and 92.3% I (R = Ph); also formed by refluxing the pyrazoline in C6H6. Thus diphenylmethylene, a catalytic pyrolysis product of Ph2CN2, in its reaction with (EtO)2P(O)CMe:CH2 displays nucleophilic nature. The normal pyrolytic reaction clearly proceeds via a pyrazoline.
- L5 ANSWER 193 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
- AN 1970:476564 CAPLUS
- DN 73:76564

- TI Reaction of optically active (1-methyl-2,2-diphenylcyclopropyl)trimethylti n with bromine or iodine
- AU Sisido, Keiiti; Miyanisi, Tokuo; Isida, Tyuzo; Kozima, Sinpei
- CS Dep. Ind. Chem., Kyoto Univ., Kyoto, Japan
- SO Journal of Organometallic Chemistry (1970), 23(1), 117-22 CODEN: JORCAI; ISSN: 0022-328X
- DT Journal
- LA English
- AB Reaction of an optically active (1-methyl-2,2-diphenylcyclopropyl) trimethyltin (I) with Br (or I) afforded 1-bromo-(or iodo)-1-methyl-2,2-diphenylcyclopropane with a small degree of retention of configuration. This is best interpreted in terms of radical mechanism for the cleavage of the cyclopropyl carbon-tin bond in I by Br or I.
- L5 ANSWER 194 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
- AN 1970:465374 CAPLUS
- DN 73:65374
- TI Insecticides applied as low-volume and conventional sprays to control larvae of the house fly in poultry houses
- AU Bailey, Donald Leroy; LaBrecque, Germain C.; Whitfield, Troy L.
- CS Entomol. Res. Div., Agr. Res. Serv., Gainesville, FL, USA
- SO Journal of Economic Entomology (1970), 63(3), 891-3 CODEN: JEENAI; ISSN: 0022-0493
- DT Journal
- LA English
- AB Small, compact spraying equipment was developed for applying low-volume and conventional insecticidal sprays by using carbon dioxide (CO2) as the propellent against larvae of Musca domestica (housefly). Field tests were made with various formulations and concns. of 6 insecticides. With conventional sprays applied at 2 g/m2, CIBA C-9491, wettable powder suspension, emulsions of dimethoate-dichlorvos mixture and Monsanto CP-51543 were the most effective; control lasted 11 days. Low-volume sprays of dimethoate and formothion at 2 or 4 g/m2 controlled the larvae 7 days.
- L5 ANSWER 195 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
- AN 1970:424804 CAPLUS
- DN 73:24804
- TI Absolute configuration of cis-2-phenylcyclopropanecarboxylic acid and related compounds
- AU Aratani, Tadatosi; Nakanisi, Yasuo; Nozaki, Hitosi
- CS Dep. Ind. Chem., Kyoto Univ., Kyoto, Japan
- SO Tetrahedron (1970), 26(7), 1675-84 CODEN: TETRAB; ISSN: 0040-4020
- DT Journal
- LA English
- Decarboxylation of (+)-cis-2-phenylcyclopropane-carboxylic acid (I) with Pb(OAc)4 in benzene or in the presence of iodine gives (-)-(1R:2R)-trans-1,2-diphenylcyclopropane and (-)-(1R:2S)-trans-2-phenylcyclopropyl iodide, resp. This establishes the absolute configuration of I as 1S:2R. Asym. synthesized (-)-(R)-2-phenylmethylenecyclopropane and (-)-(R)-phenylspiropentane are correlated with I through (+)-(1S:2R)-cis-1-methyl-2-phenylcyclopropane, whose ozonolysis affords (-)-(1R:2S)-cis-2-methylcyclopropanecarboxylic acid. (1S:2S)-trans-2-Phenylcyclopropyllithium adds to benzyne stereospecifically to produce (1S:2S) trans 1 (o lithiophenyl) 2 phenylcyclopropane.
- L5 ANSWER 196 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
- AN 1970:128048 CAPLUS
- DN 72:128048
- TI Cyclopropanes. XXVI. Electrolytic reduction of optically active 1-halo-1-methyl-2,2-diphenylcyclopropanes
- AU Webb, J. L.; Mann, Charles K.; Walborsky, H. M.
- CS Chem. Dep., Florida State Univ., Tallahassee, FL, USA
- SO Journal of the American Chemical Society (1970), 92(7), 2042-51 CODEN: JACSAT; ISSN: 0002-7863
- DT Journal
- LA English
- OS CASREACT 72:128048
- AB The electrochem. reduction of optically active 1-halo-1-methyl-2,2-

diphenylcyclopropanes was investigated by using cyclic voltammetry, controlled potential electrolysis, and stereochem. techniques. The cyclic voltammetry curves showed 3 well-defined peaks for all halides examined The nature and significance of these peaks are discussed. The controlled potential electrolyses of the halides at a Hg electrode produced complex current-time relations which are attributed to the formation of organomercurials. Reduction of optically active 1-bromo-1-methyl-2,2-diphenylcyclopropane, 1-iodo-1-methyl-2,2-diphenylcyclopropane, and 1-methyl-2,2-diphenylcyclo-propylmercuric bromide lead to 63, 53, and 100% retention of configuration, resp.

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retention of configuration, resp.
     ANSWER 197 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
L5
AN
     1970:66594 CAPLUS
DN
     72:66594
TI
     Insecticidal 1,1-diaryl-2,2-dihalocyclopropanes
IN
     Holan, George
PA
     Monsanto Chemicals (Australia) Ltd.
so
     U.S., 4 pp.
     CODEN: USXXAM
DT
     Patent
LA
     English
FAN.CNT 1
                      KIND DATE APPLICATION NO.
     PATENT NO.
                                                                 DATE
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     US 3481993
                                           US 1967-689317
PΙ
                         Α
                               19691202
                                                                  19671211 <--
PRAI AU 1966-15134
                        Α
                               19661212
     For diagram(s), see printed CA Issue.
     The title compds. (I) which are useful insecticides, especially for mosquito
AB
     larvae specie Aedes aegypti, were prepared Thus, fuming HNO3 (sp. gr. 1.5;
     13 ml) was added dropwise to a mixture of 12 ml AcOH and 20 ml Ac2O at
     <10°; in small portions 11.2 g II (Y1 = Y2 = Cl) was added with
     stirring over 1 hr at -5 to +5°; the mixture was quenched in 200 ml
     ice water to yield 90% 1,1-bis(p-nitrophenyl)-2,2-dichlorocyclo-propane,
     m. 184°. The following I were similarly prepared (Y1 and Y2 given):
     Br, Br; Cl, Br; Cl, F; and Cl, Cl.
L5
     ANSWER 198 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
AN
     1969:523330 CAPLUS
DN
     71:123330
     New inversion in the reduction of optically active cyclopropyl bromides by
ΤI
     triphenyltin hydride
     Altman, Lawrence J.; Nelson, Barbara W.
ΑU
CS
     Stanford Univ., Stanford, CA, USA
     Journal of the American Chemical Society (1969), 91(18), 5163-4
SO
     CODEN: JACSAT; ISSN: 0002-7863
DT
     Journal
LA
     English
GI
     For diagram(s), see printed CA Issue.
AB
     Mechanisms are proposed to explain the net inversion observed in the reduction
     of optically active I and II with excess Ph3SnH (reactant, temperature, product,
     rotation, and % enantiomeric excess are given): (+)-(S)-I, 80°,
     (+) - (S) - III, 0.37°, 0.29; (+) - (S) - I, 63°, (+) - (S) - III,
     1.11°, 0.87; (+)-(S)-I, 60°, (+)-(S)-III, 0.82°,
     0.65; (+) (S)-I, 40^{\circ}, (+)-(S)-III, 1.75^{\circ}, 1.38; (-)-(R)-II,
     65, (-)-(R)-IV, -4.44°, 2.28.
L5
    ANSWER 199 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
AN
     1969:513049 CAPLUS
DN
     71:113049
ΤI
    Reactions of diphenyldiazomethane with vinyl- and allylphosphonates
ΑU
     Pudovik, A. N.; Gareev, R. D.; Kuznetsova, L. I.
CS
     Kazan. Gos. Univ., Kazan, USSR
SO
     Zhurnal Obshchei Khimii (1969), 39(7), 1536-43
     CODEN: ZOKHA4; ISSN: 0044-460X
DT
    Journal
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Russian

For diagram(s), see printed CA Issue.

Adding 11.64 g. Ph2CN2 to 19.7 g. CH2:CHP(O)(OEt)2 at 80° and

heating 3-4 hrs. gave 92% N, some 8.8 g. unreacted ester, and 74.6% di-Et

LA

GI AB

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2,2-di-phenylcyclopropylphosphonate (I), m. 58.5°, b0.015
152-70° (crude). Similarly were prepared the following analogs:
di-Me, m. 74-5°; di-Pr, b0.002 163-4°, d20 1.1017,
n20D 1.5402; and di-Bu, b0·005 180-1°, 1.0771, 1.5313. When
the reaction was run in the presence of a catalytic amount CuSO4 for 30 min.
following the addition it gave 26.1% benzophenazine, m. 162°, some
unreacted vinylphosphonate, about 3.5% Ph2CO, and 24.8% I. Ph2CN2 and
CH2:CHCH2P(0)(OEt)2 mixed and heated at 140-50° as above gave 53%
N, benzophenazine, (Ph2CH)2, much unreacted ester, 1.1% Ph2CO, and 12.8%
di-Et (2,2-diphenyl-cyclopropylmethyl)phosphonate, b0.0007
157-8°, 1.1142, 1.5435. Similar reaction in the presence of CuSO4
run by mixing the reactants over 5 hrs. gave 49.7% N, 50% benzophenazine,
2.5% Ph2CO, and no phosphonate ester with the cyclopropane ring. Ph2CN2
and CH2:CHPOCl2 mixed over 4 hrs. (exotherm) at 30° (cooling) gave
98.5% N, much starting dichloride, and 81.5% 2,2-
diphenylcyclopropylphosphonic dichloride, b0.005 146-8°, -,
1.6051. To 13 g. CH2:CHPO(OEt)2 in Et2O was added at 0° 36.7 g.
Ph2CN2 in petroleum ether and kept 3 days in the cold to precipitate 72.6% II, m.
101-2°. II and CH2:CHPO(OEt)2 heated 2 hrs. at 80°, then at
180°, gave 97% N and 71.2% I. Thus, formation of I and analogs
proceeds not through II but through a diazonium mechanism. A carbene
mechanism is excluded, since Ph2CN2 is stable <85°.
ANSWER 200 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
1969:438392 CAPLUS
71:38392
Absolute configuration of cis-2-phenylcyclopropanecarboxylic acid
Aratani, T.; Nakanisi, Y.; Nozaki, Hitosi
Kyoto Univ., Kyoto, Japan
Tetrahedron Letters (1969), (22), 1809-10
CODEN: TELEAY; ISSN: 0040-4039
Journal
English
For diagram(s), see printed CA Issue.
Trans- and cis-2-phenylcyclopropanecarboxylic acids (Ia, Ib)
decarboxylated with Pb(OAc)4 in C6H6 at 80° in the presence of
Cu(OAc)2-C5H5N gave 18 and 22% yields of trans-1,-2-diphenylcyclopropane
(II). Retention of configuration at the Ph-substituted C of Ia was shown:
(+) - (1S, 2S) - Ia, [\alpha] 20D 376° (c 0.88, CHCl3) gave
(+) - (1S, 2S) - (II), [\alpha] 20D 418° (c 0.96, CHCl3). Similar
treatment of partially resolved cis-acid [(+)-Ib] [\alpha]20D 20°
(c 1.40, CHCl3)] gave the (-)-(1R,2R) isomer of II, [\alpha]20D
-266° (c 1.94, CHCl3). It was concluded that (+)-Ib should have
the absolute configuration 1S,2R. Ia and Ib treated with Pb(OAc)4 and iodine
under irradiation gave 43 and 42% yields of trans-2-phenylcyclopropyl iodide
(III), b2 77-8°. Treatment of (+)-(1S,2S)-Ia gave (+)-(1S,2S)-III,
[\alpha] 20D 188° (c 0.80, CHCl3), metalated with BuLi, carbonated,
and esterified to give the Me ester of (+)-Ia, [\alpha]20D 270° (c
1.22, alc.), showing that the Barton reaction proceeds with similar
stereochemistry as the phenylation reaction. Since iododecarboxylation of
(+)-Ib, [\alpha]20D 16° (c 1.00, CHCl3), gave (-)-(1R,2R)-III,
[\alpha] 20D -128° (c 2.06, CHCl3), the absolute configuration of
(+)-Ib was reconfirmed as 1S,2R.
ANSWER 201 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
1969:429812 CAPLUS
71:29812
Generation and trapping of an optically active free radical in the absence
of a cage. The mechanism of dissolving metal reduction of alkyl halides
Jacobus, John; Pensak, David
Princeton Univ., Princeton, NJ, USA
Journal of the Chemical Society [Section] D: Chemical Communications (
1969), (8), 400-1
CODEN: CCJDAO; ISSN: 0577-6171
Journal
English
CASREACT 71:29812
```

Reduction of optically pure (+)-(S)-1-bromo-1-methyl-2,2-diphenylcyclopropane

with Na dihydronaphthylide in dimethoxyethane yields 29% optically pure

L5

AN DN

ΤI

AU CS

SO

DT

LA

GI

AB

L5

AN DN

TI

AU

CS

SO

DΤ

LA

OS

AB

(-)-1-methyl-2,2-diphenylcyclopropane with net retention of configuration. It is proposed that this and all dissolving-metal redns. of alkyl halides proceed via an optically active free radical.

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L5 ANSWER 202 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
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AN 1969:412815 CAPLUS

DN 71:12815

TI Diphenyldichlorocyclopropane insecticides

IN Holan, George

PA Monsanto Chemicals (Australia) Ltd.

SO Pat. Specif. (Aust.), 17 pp.

CODEN: ALXXAP

DT Patent

LA English

FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
		-			
PΙ	AU 283356		19680524	UA	19631024 <
	US 3642910		19720215	US	19690617 <

GI For diagram(s), see printed CA Issue.

AB Substituted 1,1-diphenyl-2,2-dichlorocyclopro-panes (I) are prepared from the corresponding 1,1-diphenylethylenes (II) by reaction with a CCl2-generating medium. Thus a solution of 4.4 g. BrCl2CHgPh and 2.5 g. II (R1 = OMe, R2 = OEt) in 50 ml. benzene was refluxed 10 hrs., filtered, and evaporated to give I (R1 = OMe, R2 = OEt), m. 114-17°) almost quant. I (R1 = R2 = Me), m. 115°, and I (R1 = R2 = MeS), were similarly prepared In another reaction, CHCl3 was slowly added to II (R1 = R2 = OMe) in methylcyclohexane containing excess tert-BuOK at 0°, and the mixture kept at 20° overnight and worked up to give I (R1 = R2 = OMe), m. 141°. I (R1 = R2 = tolyl) was also prepared These compds. have insecticidal activity but have low toxicity to animals and economic crops. They are active against DDT-resistant insects in many cases. The compds. are best applied as an emulsion formed by addition of an organic solvent solution to H2O.

- L5 ANSWER 203 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
- AN 1969:105415 CAPLUS
- DN 70:105415
- TI Toxicity of DDT and related compounds to certain lepidopteran cotton insects
- AU Wolfenbarger, Dan A.; Lowry, William L.
- CS Entomol. Res. Div., Agr. Res. Serv., Brownsville, TX, USA
- SO Journal of Economic Entomology (1969), 62(2), 432-5 CODEN: JEENAI; ISSN: 0022-0493
- DT Journal
- LA English
- Deuterium labeled DDT, applied as a conventional low-volume spray, was the most effective of several diphenyl aliphatics against larvae of the tobacco budworm (Heliothis virescens), the bollworm (H. zea), and the cabbage looper (Trichoplusia ni). In topical applications Dilan (a mixture of 1 part of 1,1-bis(p-chlorophenyl)-2-nitropropane (Prolan) and 2 parts of 1,1-bis(p-chlorophenyl)-2-nitrobutane (Bulan), was the most toxic compound to tobacco budworm larvae, and Prolan applied topically was more toxic than Bulan to bollworm and tobacco budworm larvae. Ultra-low-volume sprays of DDT were more effective than conventional low-volume sprays to pink bollworm (Pectinophora gossypiella) adults immediately after application. The LD50 value for DDT applied topically to a strain from Ohio was 6.8 mg./g., 34 times that of the laboratory strain.
- L5 ANSWER 204 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
- AN 1969:95732 CAPLUS
- DN 70:95732
- TI Halocyclopropane insecticides and the mode of action of DDT
- AU Holan, George
- CS Div. Appl. Chem., C.S.I.R.O., Melbourne, Australia
- SO Nature (London, United Kingdom) (1969), 221(5185), 1025-9 CODEN: NATUAS; ISSN: 0028-0836
- DT Journal
- LA English

- A steric theory of DDT action led to the design of some new and highly AB active halocyclopropane insecticides. The new compds. suggest a general van der Waals model for diaryl insecticides and support a theory of insecticide action based on the Na pores of nerve membranes. The following modification of Mullins' (1954, 1956) theory is proposed. of the applied insecticide distributes itself at the lipid-protein nerve membrane interface. There, because of its 3-dimensional conformation, the base containing the phenyl rings locks itself into the overlaying protein layer by forming a mol. complex with it. The smaller apex consisting of the cyclopropane ring fits into the channel of a pore in the lipid part of the membrane. While the whole structure is locked in this position, the apex keeps the pore or receptor open to Na+, with the consequent delay in the falling phase of the Na+ potential. The hydrocarbons can be viewed as "mol. wedges" with very specific solubility, charge, and dimensional requirements.
- L5 ANSWER 205 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
- AN 1969:15824 CAPLUS
- DN 70:15824
- TI Dihedral angle and bond angle dependence of vicinal proton-fluorine spin-spin coupling
- AU Williamson, Kenneth L.; Hsu, Yuan-Fang Li; Hall, Frances H.; Swager, Susan; Coulter, Margaret S.
- CS Mount Holyoke Coll., South Hadley, MA, USA
- SO Journal of the American Chemical Society (1968), 90(24), 6717-22 CODEN: JACSAT; ISSN: 0002-7863
- DT Journal
- LA English
- OS CASREACT 70:15824
- AB From an anal. of the N.M.R. spectra of compds. of fixed and known stereochemistry, the vicinal proton-F coupling constant was found to be a function of dihedral angle; the dependence is like vicinal JHH, a maximum at 0° (.apprx.31 Hz.), a min. at 90° (.apprx.0 Hz.), and a maximum at 180° (.apprx.44 Hz.), and not a linear dependence as has been reported. JHF-vic is extremely dependent on bond angle, being .apprx.31 Hz. for a bond angle near 109° and dropping to 0.9 Hz. for a bond angle near 118° (dihedral angle fixed at 0°). Evidence is presented for a bond length dependence of JHF-vic.
- L5 ANSWER 206 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
- AN 1968:495768 CAPLUS
- DN 69:95768
- TI Cyclopropanes. XXIV. Sodium-liquid ammonia reduction of optically active cyclopropyl halides
- AU Walborsky, Harry M.; Johnson, F. P.; Pierce, J. B.
- CS Florida State Univ., Tallahassee, FL, USA
- SO Journal of the American Chemical Society (1968), 90(19), 5222-5 CODEN: JACSAT; ISSN: 0002-7863
- DT Journal
- LA English
- The reduction of (-)-(R)-1-halo-1-methyl-2,2-diphenylcyclopropane leads to the formation of optically active (+)-(S)-1-methyl-2,2-diphenylcyclopropane (I) with over-all retention of configuration, as well as 2 ring-opened products, 1,1-diphenyl-2-methylpropane and 1,1-diphenylbutane. The amount of optical activity observed in I is dependent on the nature of the starting halogen (Cl > Br > I), the concentration of the Na in liquid NH3 solution, and a heterogeneity factor.
- L5 ANSWER 207 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
- AN 1968:451154 CAPLUS
- DN 69:51154
- TI The comparative toxicity of DDT and analogs to susceptible and resistant houseflies and mosquitoes
- AU Metcalf, R. L.; Fukuto, T. R.
- CS Univ. of California, Riverside, CA, USA
- SO Bulletin of the World Health Organization (1968), 38(4), 633-47 CODEN: BWHOA6; ISSN: 0366-4996
- DT Journal
- LA English

GI For diagram(s), see printed CA Issue.

Analogs of DDT were studied for their comparative toxicities to AB susceptible and insecticide-resistant houseflies (Musca domestica) and mosquitoes (Culex pipiens fatigans and Anopheles albimanus). I (R = OH), b0.4 160°, was prepared by the Grignard reaction between p-ClC6H4MgBr and Et pivalate. This was then reacted with PBr3 and reduced to give I (R = H), b0.2 128°, m. 76-8°. 1,1-Bis(pchlorophenyl)cyclopropane (m. 100-3°), 1,1-bis(pchlorophenyl)methylcyclopropane (b0.15 135-8°), and 2,2-bis(p-chlorophenyl)-1,1,1-trifluoroethane were also prepared In the series of 120 compds., the relative effectiveness against DDT-resistant insects was correlated with the susceptibility of the mols. to attack at the benzylic H by DDTase. Compds. especially effective against the resistant insects were those in which this detoxification mechanism was blocked by o-chlorination, α -fluorination, or by alteration of the aliphatic portion of the mol.

L5 ANSWER 208 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN

AN 1968:402360 CAPLUS

DN 69:2360

TI Cyclopropanes. XXIII. An optically active cyclopropylsodium

AU Pierce, James B.; Walborsky, H. M.

CS Florida State Univ., Tallahassee, FL, USA

SO Journal of Organic Chemistry (1968), 33(5), 1962-5 CODEN: JOCEAH; ISSN: 0022-3263

DT Journal

LA English

GI For diagram(s), see printed CA Issue.

AB Halogen-metal exchange between (-)-(R)-1-bromo-1-methyl-2,2-diphenylcyclopropane and n-amylsodium yielded upon carbonation (+)-(R)-1-methyl-2,2-diphenylcyclopropanecarboxylic acid (I) (optical purity, 46%), (+)-(S)-1-methyl-2,2-diphenylcyclopropane (II) (optical purity, 83%), and (-)-(R)-n-penty-1-methyl-2,2-diphenylcyclopropane (III) (optical purity, 66%) with over-all retention of configuration. The most effective method for the reduction of a vinylcyclopropane intermediate was by the use of the diimide. 20 references.

- L5 ANSWER 209 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
- AN 1968:90257 CAPLUS
- DN 68:90257
- TI Catalytic hydrogenation and hydrogenolysis by pentacyanocobaltate(II)
- AU Kwiatek, Jack; Seyler, Jay K.
- CS U.S. Ind. Chem. Co., Div. of Nat. Distillers, and Chem. Corp., Cincinnati, OH, USA
- SO Advances in Chemistry Series (1968), No. 70, 207-32 CODEN: ADCSAJ; ISSN: 0065-2393
- DT Journal
- LA English

Radical intermediates are indicated both in the hydrogenolysis of organic halides and in the hydrogenation of certain activated C-C double bonds catalyzed by Co(CN)53-. In both cases, formation of the reduced substrate occurs by H transfer from Co(CN)5H3- to the radical. In the absence of excess Co(CN)5H3-, the radicals either disproportionate or form stable organocobalt complexes by reaction with Co(CN)53-. Addition of Co(CN)5H3- to other activated C-C double bonds results in the formation of stable organocobalt complexes, via a nonradial mechanism. Evidence is presented for the formation of N-amidocobalt complexes. RCONHCo(CN)53-, from certain α -halo and α , β -unsatd. nitriles. The relation of structure to the stability and catalytic activity of organocobalt complexes is discussed. 62 references.

- L5 ANSWER 210 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
- AN 1968:86475 CAPLUS
- DN 68:86475
- TI Solvolysis of cyclopropyl halides. 2-Phenylcyclopropyl chlorides
- AU Hausser, Jack W.; Pinkowski, Norman J.
- CS Duquesne Univ., Pittsburgh, PA, USA
- SO Journal of the American Chemical Society (1967), 89(26), 6981-4 CODEN: JACSAT; ISSN: 0002-7863

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LA
     English
AB
     cis- and trans-2-Phenylcyclopropyl chloride and 2,2-diphenylcyclopropyl
     chloride have been solvolyzed in AcOH. The products of solvolysis in all
     cases are the corresponding ring-opened allylic acetates.
                                                                The relative
     rates at 150° and the activation parameters are presented.
                                                                 These
     results are considered in terms of the electronic and steric requirements
     of electrocyclic ring-opening processes. Two alternative interpretations
     are presented. 19 references.
     ANSWER 211 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
L5
     1968:49141 CAPLUS
AN
DN
     68:49141
     Reaction of aryl-substituted ethylenes with dihalocarbenes
ΤI
     Nefedov, O. M.; Shafran, R. N.
ΑU
     Zhurnal Obshchei Khimii (1967), 37(7), 1561-6
SO
     CODEN: ZOKHA4; ISSN: 0044-460X
DT
     Journal
LA
     Russian
AB
     Rates of addition of CCl2 and CBr2 carbenes to various arylethylenes were
     reported in reactions of CHCl3 and CHBr3 in cyclohexene, arylethylenes,
     and Me3COK at -10° to -15° run on a competitive basis. The
     following relative reaction rates with cyclohexene as the reference
     substance were observed for indicated arylethylenes: (a) addition of CCl2:
     styrene, 1.4; \alpha-methylstyrene, 2.2; Ph2C:CH2, 1.8-1.9;
     p-MeC6H4CH:CH2, 1.5; mixed isomers, 1.5; mixed isomeric vinylxylenes, 1.5;
     vinylmesitylene 1.4; (b) addition of CBr2: 0.42; 3.3; 1.1; -; -; 0.13,
     resp. The following products were isolated and tested as herbicides; the
     most effective was 1,1-diphenyl-2,2-dichlorocyclopropane, which had especially
     strong activity against kidney bean plants on contact or systemically.
     1-Phenyl-2,2-dichlorocyclopropane, b19 114.5-15°, n20D 1.5518, d20
     1.2310; 1-phenyl-1-methyl-2,2-dichloro analog, b18 117-18°, 1.5412,
     1.1831; 1,1-diphenyl-2,2-dichloro analog, m. 107-8°;
     1-(p-toly1)-2,2-dichlorocyclopropane, b13 121-2°, 1.5454, 1.1868;
     1-tolyl-2,2-dichloro analog mixed isomers b6.5 107.5-8.5°, 1.5470,
     1.1919; 1-xylyl-2,2-dichloro analog (mixed isomers), b7 108-10°,
     1.5470, -; 1-mesityl-2,2-dichloro analog, b0.9 101.5-2°, 1.5476,
     1.1611; 1-phenyl-2,2-dibromocyclopropane, b2.8 101.5-2°, 1.5992,
     1.7383; 1-phenyl-1-methyl-2,2-dibromo analog, b2.8 105°, 1.5855,
     1.6506; 1,1-diphenyl-2,2-dibromo analog, m. 77-8°;
     1-p-toly1-2,2-dibromo analog, b0.9 100-100.5°, 1.5918, 1.6543.
L5
     ANSWER 212 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
AN
     1967:453734 CAPLUS
DN
     67:53734
     Simple preparation of 1,1-dihalocyclopropanes
TТ
     Weyerstahl, Peter; Klamann, Dieter; Finger, Carl; Nerdel, Friedrich;
ΑU
     Buddrus, Joachim
     Esso-Forschungslab., Hamburg-Harburg, Fed. Rep. Ger.
CS
     Chemische Berichte (1967), 100(6), 1858-69
SO
     CODEN: CHBEAM; ISSN: 0009-2940
DТ
     Journal
     German
LA
GΙ
     For diagram(s), see printed CA Issue.
     Preparation of 1,1-dihalocyclopropanes (I) from olefins, trihalomethanes, and
AB
     ethylene oxide in the presence of a quaternary salt catalyst (e.g.,
     Et4NBr) is described. The reaction proceeded via a transition dichloro-,
     fluorochloro-, and difluorocarbene.
     ANSWER 213 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
L5
AN
     1967:95170 CAPLUS
DN
     66:95170
     Chloroalkyllithium compounds
ΤI
PA
     Borg-Warner Corp.
SO
     Neth. Appl., 12 pp.
     CODEN: NAXXAN
DТ
     Patent
LA
    Dutch
FAN.CNT 1
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DT

Journal

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APPLICATION NO.
                       KIND DATE
     PATENT NO.
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PΙ
                                19661129
                                            NT.
     NL 6604777
                                                                              < - -
     FR 1470982
                                            FR
     GB 1131860
                                             GB
     US 3439053
                                            US
                                                                    19650528 <--
                                19690415
                                19650528
PRAI US
     PhCCl2Li (I) was prepared by adding 0.043 mole BuLi within 10 min. at
AB
     -90° to 7.34 g. PhCHCl2 (or 8.45 g. PhCCl3) in 100 ml.
     tetrahydrofuran. After 15 min. the mixture was poured onto solid CO2.
     After evaporation of the CO2, C6H6, water, and base were added, and the aqueous
     phase was separated, acidified, and extracted with Et2O to give 42% BzCO2H. When
     40 ml. Me2C:CMe2 was added to I, a deep-red color developed at -65 to
     -40°, and 48% 1-chloro-1-phenyltetramethylcyclopropane was
     isolated, m. 65-7° (petroleum ether). With MeI, I reacted to give
     77% PhCCl2Me. Similarly, Cl3CLi was prepared from CHCl3 or CCl4; with CO2
     it gave 76% Cl3CCO2H, with cyclohexene 60% 7,7-dichloronorcarane, with
     Ph2C:CH2 52% 1,1-dichloro-2,2-diphenylcyclopropane, m. 113-14°.
     Similar reactions of BuLi with Ph2CCl2 (producing 40% Ph2CClLi) and with
     CH2Cl2 (producing 60% Cl2CHLi) were described.
     ANSWER 214 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
L5
AN
     1967:95144 CAPLUS
DN
     66:95144
     Optically active organotin compounds. I. Preparation and reaction of
ΤI
     (1-methyl-2,2-diphenylcyclopropyl)trimethyltin
AU
     Sisido, Keiiti; Kozima, Sinpei; Takizawa, Koiti
CS
     Univ. Kyoto, Kyoto, Japan
     Tetrahedron Letters (1967), (1), 33-6
SO
     CODEN: TELEAY; ISSN: 0040-4039
DT
     Journal
LA
     English
os
     CASREACT 66:95144
GI
     For diagram(s), see printed CA Issue.
     Treatment of (+) - (S) -1-bromo-1-methyl-2,2-diphenylcyclopropane (I),
AB
     [\alpha] 19D 32°, with Me3SnLi (II) 15 hrs. at 0° in
     tetrahydrofuran (N atmospheric) and separation of the products by preparative gas
     chromatog. in He (100 ml./min.) over Thermol-3 at 170° gave 44.1%
     (+)-(1-methyl-2,2-diphenylcyclopropyl)trimethyltin (III), [a]21D
     11.6° (c 1.45, CHCl3), n21D 1.5742; and 37% (-)-(R)-1-methyl-2,2-
     diphenylcyclopropane (IV), [\alpha]21D -39.0° (c 1.12, CHCl3). Retention times for I, III, and IV were 10.5, 26.0, and 5.5 min., resp.
     Essentially the same reaction was carried out with (-)-(R)-1-bromo-1-
     methyl-2,2-diphenylcyclopropane to yield 61.2% III, [α]D
     -16.1°, and 17.2% IV, [\alpha]D 51.3°. IV had the same
     absolute configuration and optical purity as I but was not formed by reduction of
     I by Me3SnH. The reaction of II with I might produce 1-methyl-2,2-
     diphenylcyclopropyllithium (V) through a 4-centered transition state (VI).
     Treatment of (+)-III with concentrated HCl in CCl4 gave (-)-(R)-IV, [\alpha]23D
     -39.5° (c 0.53, CHCl3) with the optical purity and absolute
     configuration of I, indicating that both the formation of the Sn-C bond
     from I and the cleavage reaction with HCl proceeded by an ionic mechanism.
     On account of the large barrier to inversion in these cyclopropane derivs.
     the Sn-C bond formation would be preceded via SE1 reaction shown as VII.
     From this it was concluded that both formation and cleavage proceeded with
     complete retention and the absolute configuration of III could be decided.
     Treatment of (+)-III with iodine in CCl4 gave 11.1% racemic
     1-iodo-1-methyl-2,2-diphenylcyclopropane, m. 89°, showing that
     cleavage proceeded via free radical mechanism. The SN1 mechanism would
     not be considerable, since cleavage by HCl proceeded by the ionic route
     with retention of configuration.
     ANSWER 215 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
L5
AN
     1967:37234 CAPLUS
DN
     66:37234
     Dihedral angle and bond angle dependence of vicinal proton-fluorine
TΙ
     spin-spin coupling
```

Williamson, Kenneth Lee; Li, Yuan-Fang; Hall, Frances H.; Swager, Susan

Mt. Holyoke Coll., South Hadley, MA, USA

AU

CS

DATE

- SO Journal of the American Chemical Society (1966), 88(23), 5678-80 CODEN: JACSAT; ISSN: 0002-7863
- DT Journal
- LA English
- GI For diagram(s), see printed CA Issue.
- The conformationally rigid mols. in which the vicinal proton and F atoms AB are held in fixed and known conformations (I-VI) were synthesized, and vicinal proton-F spin-spin coupling consts. were determined The dihedral angle dependence of JHF(vic) was similar to that of JHH'(vic), and was not a linear function of the dihedral angle. The vicinal proton-F coupling constant is probably dependent on the electronegativity of adjacent substituents and on the bond length. JHF(vic) in saturated systems is dependent on the angels θ and θ ' in a manner predicted by Karplus (CA 59, 14770f) for JHH'. I was prepared by Diels-Alder condensation of CH2:CHF with hexachlorocyclopentadiene. II was prepared by reaction of anthracene and fluoromaleic anhydride (VII) and was esterified to III. Diels-Alder condensation of VII and furan gave IV, which on hydrolysis gave the exo diacid. V. VI was prepared by addition of flurochlorocarbene to 1,1-diphenylethylene. All the coupling consts. were pos.
- L5 ANSWER 216 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
- AN 1967:18572 CAPLUS
- DN 66:18572
- TI 1,1-Dichloro-2,2-bis(4-chlorophenyl)cyclopropane
- IN Wiles, Robert A.
- PA Allied Chemical Corp.
- SO U.S., 2 pp.
- CODEN: USXXAM
- DT Patent
- LA English
- FAN.CNT 1

PATENT NO. KIND DATE APPLICATION NO. DATE

US 3285811 19661115 US 1965-478009 19650630 <--

- PI US 3285811 19661115 US 1965-478009 19650630 <-AB The title compound (I) was prepared by addition of:CCl2 to (p-ClC6H4)2C:CH2 (II).
 Thus, 27.5 g. II and 70.9 g. bis(2-methoxyethyl) ether was heated under N
 to 100-5° and 41 g. Cl3CCO2Na was added over 0.5 hr. Heating was
 continued until CO2 evolution stopped and the mixture cooled and poured into
 1 l. H2O to give an oil which crystallized to give 27% I, m. 129-34°
 (ACOH). I had insecticidal activity (tests given).
- L5 ANSWER 217 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
- AN 1966:490143 CAPLUS
- DN 65:90143
- OREF 65:16835b-c
- TI The stereochemistry of electroreductions. I. Cyclopropyl halides
- AU Annino, Raymond; Erickson, Ronald E.; Michalovic, John; McKay, Bruce
- CS Canisius Coll. Buffalo, NY
- SO Journal of the American Chemical Society (1966), 88(19), 4424-8 CODEN: JACSAT; ISSN: 0002-7863
- DT Journal
- LA English
- AB The electrochem. behavior of optically active 1-bromo-2,2-diphenylcydopropanecarboxylic acid, its Me ester, and 1-bromo-1-methyl-2,2-diphenylcyclopropane-carboxylic acid, its Me ester, and 1-bromo-1-methyl-2,2-diphenylcyclopropane is reported. Reduction of the acid or its Me ester yields products of partially inverted configuration, whereas the redns. of the carboxylate ion and 1-bromo-1-methyl-2,2-diphenylcyclopropane proceed with partial retention of configuration. The stereochem. results correspond closely with those observed in Zn metal redns. of the same compds. They are readily interpreted in terms of a mechanism involving initial attack by the electrode or metal surface on the halogen side of the carbon-halogen bond. 29 references.
- L5 ANSWER 218 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
- AN 1966:411953 CAPLUS
- DN 65:11953
- OREF 65:2152f-g

- TI Cyclopropanes. XX. Electrochemical reduction of (+)-S-1-bromo-1-methyl-2,2diphenylcyclopropane AII Mann, C. K.; Webb, J. L.; Walborsky, H. M. CS Florida State Univ., Tallahassee SO Tetrahedron Letters (1966), (20), 2249-55 CODEN: TELEAY; ISSN: 0040-4039 DT Journal English LA cf. CA 64, 633h. The controlled potential electrolysis of AB (\pm) -1-bromo-1-methyl-2,2-diphenylcyclopropane (I) (0.003-0.010M in 0.10M [Et4N]Br in MeCN) using compartmented cells and 3-electrode configurations at -2.7 v. yielded 93% 1-methyl-2,2-diphenyl-cyclopropane (II) with 1.98 ± 0.3 electrons/mol. reacted. (+)-I gave similarly (-)-II, [α]5461 -38.1° (25% optical purity) (63% retention of configuration). (+)-I reduced with Li gave (-)-II with 46% retention of activity and reduced with Mg resulted in 13-18% retention of activity with overall retention of configuration. L5 ANSWER 219 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN AN 1966:3828 CAPLUS DN64:3828 OREF 64:633h,634a Cyclopropanes. XIX. Reaction of lithium metal with optically active ΑU Walborsky, H. M.; Aronoff, M. S. CS Florida State Univ., Tallahassee SO Journal of Organometallic Chemistry (1965), 4(5), 418-20 CODEN: JORCAI; ISSN: 0022-328X DT Journal LA English cf. CA 62, 7606a. Direct metalation of (+)-(S)-1-bromo-1-methyl-2,2-AΒ diphenylcyclopropane with Bu-Li yields the corresponding Li derivative which is partially racemized. The amount of racemization is dependent upon the nature of the halogen substituent and also on the percentage of Na in the Li and the particle size of the Li. With constant Na content and Li particle size the racemization was 64% for I, 58% for Br, and 34% for Cl
- and with 0.002%, 0.02%, and 1% Na content, carbonation of reaction mixtures yielded 1-methyl-2,2-diphenyl-cyclopropanecarboxylic acid with optical purity of 13%, 16% and 36%, respectively.
- DN 63:72114 OREF 63:13301c-e Preparation and chemistry of α -chloroalkyllithium compounds. Their role as carbenoid intermediates Hoeg, Donald F.; Lusk, Donald I.; Crumbliss, Alvin L. ΑU
- CS Borg-Warner Res. Center, Des Plaines, IL

ANSWER 220 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN

- SO Journal of the American Chemical Society (1965), 87(18), 4147-55 CODEN: JACSAT; ISSN: 0002-7863 DTJournal
- LAEnglish os CASREACT 63:72114

1965:472114 CAPLUS

L5

AN

AΒ The reaction of polychloromethanes with n-butyllithium in tetrahydrofuran at low temperatures (-100°) via α -metalation or halogen-metal interconversion has been used to prepare a new class of organolithium reagents, α -chloroalkyllithium compounds. The procedure was based on our observation of the remarkable stabilizing influence of tetrahydrofuran on α -chloroalkyllithium structures. At low temperatures, these compounds behave as typical organolithium structures and have been characterized by hydrolysis, deuterolysis, and direct carbonation to the corresponding acids (or derivatives). They react (couple) readily with the more reactive alkyl halides, presumably via nucleophilic displacements of the chloro carbanion on carbon. While these compounds were indefinitely stable at -100°, they decomposed spectacularly above -65°, suggestive of carbene formation via elimination of LiCl. If olefins were present during this decomposition (they were added without evidence of reaction at -100°), good yields of the corresponding cyclopropanes were obtained from

 α, α -dichlorobenzyllithium and trichloromethyllium. In contraindication of a free carbene mechanism in the formation of the cyclopropanes, however, the stability of α -chloroalkyllithium compounds appears influenced by the more nucleophilic olefins, suggestive of a direct reaction of the olefin with the organolithium compound (or its structural equivalent), the reactivity (nucleophilic olefin sequence) and specificity in qualitative accord with results previously thought indicative of a free carbene intermediate. Several mechanisms are considered in the light of these results.

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ANSWER 221 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
L5
AN
     1965:454374 CAPLUS
     63:54374
DN
OREF 63:9862g-h,9863a
     Insecticides
ΤI
     Monsanto Chemicals (Australia) Ltd.
PA
SO
     16 pp.
ידת
     Patent
     Unavailable
LA
```

FAN.CNT 1

	PATENT NO.	KIND DATE	DATE	APPLICATION NO.	DATE
PI	NL 6412298		19650426	NL	. <
PRAT	Γ ΔΙΙ		19631024		

For diagram(s), see printed CA Issue.

GΙ Insecticidal 1,1-[bis(4-halophenyl)]-2,2-dichlorocyclopropanes, I, where R ΑB and R' are identical or different and designate Cl, Br, or I, prepared by treating the corresponding 1,1-bis(p-substituted phenyl)ethene with phenyl(trichloromethyl)mercury (II) or phenyl(bromodichloromethyl)mercury. Thus, 3.97 g. II, and 1.77 g. 1,1-bis(p-chlorophenyl)-ethene were refluxed in 50 cc. benzene 36 hrs. and filtered to eliminate phenylmercuric chloride. The filtrate was evaporated and the residue recrystd. from petr. ether (b. 40-60°) and MeOH, to give 1.66 g. I, where R and R' are Cl, yield 96.4%, m. 131-2°. Similarly prepared were I, where R and R' are F (m. 114°) and where R and R' are Br (m. 136°). Dispersions of I are used against DDT-resistant insects, especially against Aedes aegypti, Prodenia eridania, and Musca domestica, and have low toxicity against warm blood animals and culture plants.

ANSWER 222 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN L5

1964:454453 CAPLUS AN

DN 61:54453 OREF 61:9384a-b

Cyclopropanes. XVI. Optically active Grignard reagent and the mechanism of TТ Grignard formation

Walborsky, H. M.; Young, A. E. ΑU

Journal of the American Chemical Society (1964), 86(16), 3288-96 SO CODEN: JACSAT; ISSN: 0002-7863

DT Journal

Unavailable LA

The reaction of (+)-(S)-1-broml-1-methyl-2,2-diphenylcyclopropane with Mg AB leads to the formation of an optically active Grignard reagent since on carbonation (-)-(S)-1-methyl-2,2-diphenylcyclopropanecarboxylic acid (12 \pm 2% optical purity) and (-)-(R)-1-methyl-2,2-diphenylcyclopropane (10 ± 2% optical purity) are isolated. Evidence is presented to show that the extensive racemization observed in the products occurs in the Grignard formation step and not after the Grignard reagent is formed. A mechanism for Grignard formation, which is consistent with the stereochem. observations, is suggested.

ANSWER 223 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN L5

AN1964:454452 CAPLUS

DN 61:54452

OREF 61:9383h,9384a

Cyclopropanes. XV. The optical stability of 1-methyl-2,2-TТ diphenylcyclopropyllithium

Walborsky, H. M.; Impastato, F. J.; Young, A. E. ΑU

CS Florida State Univ., Tallahassee

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DT
     Journal
LA
     Unavailable
     cf. CA 61, 6898c. Halogen-Li interchange between (+)-(S)-1-bromo-1-methyl-
AB
     2,2-diphenylcyclopropane and BuLi produced 1-methyl-2,2-
     diphenylcyclopropyllithium which on treatment with CO2, Br, and I yielded
     products in which the configuration as well as the optical activity had
     been completely retained. No effect on the optical results could be found
     on varying the temperature, solvent, or reaction time. The Li derivative was found
     to react with solvent in the order 1,2-dimethoxyethane < tetrahydrofuran <
     Et20.
     ANSWER 224 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
L5
AN
     1964:2795 CAPLUS
DN
     60:2795
OREF 60:417d-h,418a-h
     Synthesis of allenes from 1,1-dihalocyclopropane derivatives and
ΤI
     alkyllithium
ΑU
     Skatteboel, Lars
     Univ. Carbide European Res. Assoc., Brussels, Belg.
CS
     Acta Chemica Scandinavica (1963), 17(6), 1683-93
SO
     CODEN: ACHSE7; ISSN: 0904-213X
DT
     Journal
LA
     English
     1,1-Dibromocyclopropane derivs. reacted with BuLi or MeLi to give allenes
AB
     in good yields. The dichloro analogs reacted similarly with BuLi, but not
     with MeLi under the same conditions. The mechanism of the reaction was
     discussed. In some cases, where the product consisted of a mixture of
     isomers, this was explained by assuming a carbene intermediate in the
               (All reactions were carried out under N; anal. gas
     chromatograms were determined on an 8.5-ft. column of squalane on chromosorb W,
     unless otherwise stated, with He as carrier gas; preparative scale gas
     chromatographic sepns. were carried out on a column of Apiezon J on
     firebrick with N or He as carrier gas; ultraviolet spectra were determined in
     hexane, unless otherwise stated). 1,1-Dihalocyclopropanes were prepared by
     the method of Doering and Hoffmann (CA 49, 15805b); equimolar amts. of
     olefin and haloform were generally used. Haloform added slowly during 6-8
     hrs. to a stirred slurry of tert-BuOK, the olefin, and dry pentane (50-100
     ml./mole olefin) at -10° to 0°, the mixture stirred overnight
     at room temperature and treated with H2O, and the product extracted with Et2O gave
     the following cyclopropane derivs. (compound, b.p./mm., m.p., nD/temperature, %
     yield given): 1,1-dibromo-2,2-dimethylcyclopropane (I), 51-2°/16,
     -, 1.5156/20°, 80; 1,1-dibromo-2,2,3-trimethylcyclopropane (II),
     65-74°/18, -, 1.5130, 27°, 84; 1,1-dichloro-2,2,3-
     trimethylcyclopropane, 63°/45, -, 1.4545/28°, 70;
     1,1-dibromo-2,2,3,3-tetramethylcyclopropane (III), -, 81°, -, 80;
     1,1-dichloro-2,2,3,3-tetramethylcyclopropane (IV), -, 52°, -, 78;
     1,1-dibromo-2-hexylcyclopropane (V), 70°/0.1, -, 1.4940/23°,
     44; 1,1-dichloro-2-hexylcyclopropane, 85°/11, -, 1.4515/24°,
     15 (low yield partly due to accidental loss of product);
     7,7-dibromobicyclo [4.1.0] heptane, 110°/12, -, 1.5577/22°
     73; 8,8-dibromobicyclo[5.1.0]octane, 60-1° /0.1, -,
     1.5521/23°, 58; 9,9-dibromobicyclo[6.1.0] nonane (VI),
     80-2°/0.1, -, 1.5520/20°, 65; 1,1-dibromo-2-
     diphenylcyclopropane (VII), 90-1°/0.1, -, 1.6001/22°, 37;
     1,1-dibromo-2,2-diphenylcyclopropane (VIII), -, 154-6°, -, 54;
     1,1-dichloro-2,2-diphenylcyclopropane, -, 115-16° -, 60;
     1,1-dibromo-2- methyl-2-(ethoxymethyl)cyclopropane (IX), 52-3°/2,
     -, 1.5024/26°, 58. A mixture of tert-BuOK (from 23 g. K), 27 g.
     1,5-cyclooctadiene, and 100 ml. dry pentane cooled in an ice-salt bath
     treated dropwise during 7 hrs. with 127 g. CHBr3 with stirring, kept
     overnight at room temperature, and treated with H2O, the precipitate filtered off,
     washed with a little Et20, the aqueous phase extracted with Et20, and the exts.
     washed with H2O until neutral, dried, and fractionated gave 21 g.
     9,9-dibromobicyclo[6.1.0]non-4-ene (X), b0.3 86°, n17D 1.5727; the
     crystalline distillation residue combined with the above precipitate and recrystd. from
     CH2Cl2 gave 38 g. 5,5,10,10-tetrabromotricyclo[7.1.0.04.6] decane (XI), m.
     174-80°. A mixture of tert-BuOK (from 13 g. K), 17.5 g.
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Journal of the American Chemical Society (1964), 86(16), 3283-8

CODEN: JACSAT; ISSN: 0002-7863

SO

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1,8-cyclotetradecadiene, and 60 ml. pentane cooled in an ice-salt bath
treated dropwise with stirring during 5 hrs. with 46.5 g. CHBr3 and kept
overnight at room temperature, H2O added, and the precipitate filtered off, washed with
a little Et2O, and recrystd from CH2Cl2 gave 10.4 g. 8,8,16,16-
tetrabromotricyclo[13.1.0.07.9]hexadecane (XII), m. 200-4°.
General procedure. 1,1-Dibromo- or 1,1-dichlorocyclopropane derivative (0.1
mole) diluted with 25 ml. dry Et2O, cooled to -40 to -30° in a dry
ice-Me2CO bath, treated dropwise with stirring during 30 min. with 0.12
mole alkyllithium in Et20, and stirred 30 min., H2O added, the Et20 layer
separated, the aqueous layer extracted with a small amount Et20, and the combined organic
solns. washed with H2O until neutral, dried, and fractionated through a
25-cm. column packed with Dixon rings or a 100-cm. spinning-band column
gave the allene; practically similar results were obtained on a larger or
smaller scale. From I and MeLi was prepared H2C:C:CMe2, 92% yield estimated by
gas chromatography (GC); a sample obtained by preparative GC b.
40°, n24D 1.4152, v 1930 and 845 cm.-1 From II and MeLi was
prepared 69% Me2C:C:CHMe, b. 72°, n25D 1.4340, 99% purity (by GC),
v 1965 cm.-1; with BuLi was obtained 68% of the allene. V and MeLi
gave 89% H2C:C: CHCH2Am, b15, 45°, n23D 1.4432, v 1950 and 842
cm.-1, containing 3% impurities (by GC). IX and MeLi gave 71%
EtOCH2CMe:C:CH2, b. 112°, n21D 1.4260, v 1955, 870, and 850
cm.-1, at least 99% purity by GC on dinonyl phthalate on Embacel. VII and
MeLi at -60° gave 82% PhCH:C:CH2, b11 64-5°, n24D 1.5809,
\lambda (EtOH) 284 m\mu (\epsilon 16,300), \nu 1940 and 860 cm.-1, at
least 99% purity by GC; rapidly oxidized in air, fairly stable (70%
recovery) when stored over hydroquinone at 0° for over a year.
VIII and MeLi gave 43% Ph2C:C:CH2, b0.01 80°, n20D 1.6301, v
1940 and 855 cm.-1, probably containing Ph2CHC: CH (weak band at 3300 cm.-1);
the distillation residue dissolved in C6H6 and the solution diluted with petr. ether
gave an unidentified compound, C45H36, m. 192-3°, mol. weight 559. VI
and MeLi gave 93% 1,2-cyclononadiene, b16 62-3°, n20D 1.5060, at
least 99% purity by GC, which (1 g.) was ozonized in EtOAc and then
oxidized with AeO2H to give 0.35 g. suberic acid, m. 138-40°. X
and MeLi gave 80% 1,2,6-cyclononatriene, unstable, b13 61-2°, n24D
1.5218, whose infrared (IR) spectrum was recorded, which (1 g.) was
ozonized in EtOAc at 0° followed by oxidin. with AcO2H to give 0.3
q. succinic acid. XI (22.6 g.) in 25 ml. dry Et20 treated dropwise at
-40° during 30 min. with 80 ml. 1.5M Et20-MeLi with stirring and
stirred 30 min., H2O added, the Et2O layer separated from insol. matter,
washed neutral with H2O, dried, and evaporated in vacuo, the residue extracted
with pentane (considerable undissolved residue remained), the extract evaporated
in vacuo, the residue distilled at 80° (bath)/0.05 mm., into a cooled
receiver, and the partly crystalline distillate recrystd. from a little pentane
gave 800 mg. 1,2,6,7-cyclodecatetraene, m. 36°, mol. weight (mass
spectrometry) 132, whose IR spectrum was recorded. XII (7.7 g.) suspended
in 10 ml. dry Et2O treated dropwise during 30 min. with 30 ml. 1.15M
Et20-MeLi at -40° with stirring, stirred 1 hr. while the bath temperature
rose to 0°, H2O added, and the Et2O phase separated, washed neutral
with H2O, dried, and evaporated in vacuo gave 1.6 g. 1,2,9,10-
cyclohexadecatetraene, m. 80° (EtOH, then pentane), whose IR
spectrum was recorded. III (25.6 g.) suspended in 50 ml. dry Et20 treated
dropwise at -40° during 1 hr. with 80 ml. 1.5M Et2O-MeLi with
stirring, stirred 30 min., H2O added, the Et2O phase separated, the aqueous phase
extracted with a little Et20, and the combined organic solns. washed neutral with
H2O, dried, and fractionated gave 6.7 g. liquid, b. 83-5°, n20D
1.4253, consisting of 3 compds. by GC. The main component, which
represented about 95% of the total mixture, was purified by preparative GC
to give 1-methyl-l-isopropenylcyclopropane (XIII), b. 84°, n25D
1.4223, v 3080, 1650, 1022, 892 cm.-1, its nuclear magnetic resonance
spectrum showing 5 bands with relative peak areas 2:3:3:2:2 with \tau =
5.30 (multiplet) (H2C:C), 8.37 (quadruplet) (C:CMe), 8.88 (singlet) (Me on
cyclopropane), and 9.40 and 9.62 (multiplets) (cyclopropane CH2);
identical (IR spectrum) with synthetic XI (see below). Ozonolysis of XIII
gave HCHO, characterized as the 2,4-dinitrophenylhydrazine (DPH) derivative,
and ketone C6H10O, characterized as the DPH derivative, m. 164-8°.
Variation of the reaction temperature between -78° and 0° or use
of dioxane, tetrahydrofuran, diglyme, or C6H6 as solvent for III gave XIII
as practically the sole product. The same result was obtained with IV and
BuLi. Also IV and BuLi yielded practically only XIII. Zn-Cu couple
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(prepared from 42 g. Zn), 134 g. CH2I2, 300 mg. iodine, and 400 ml. dry Et2O refluxed 30 min., treated dropwise during 0.75 hr. with 77 g. H2C:CMeCMe:CH2, refluxed 62 hrs., and filtered, and the filtrate washed with dilute HCl and aqueous NaHCO3, dried, and fractionated gave 9.8 g. 60:40 mixture of 2 compds., b. 85-92°, n24D 1.4245, which were separated by preparative GC to give (as the main product) XIII, b. 84°, n25D 1.4223; the other component was probably 1,1'-dimethylbicyclopropyl, n25D 1.4228, v 3020 and 1012 cm.-1

ANSWER 225 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN 1963:447960 CAPLUS 59:8614b-d

L5 AN DN OREF 59:8614b-d Reactions related to the addition of dichlorocarbene to norbornylene ΤI AU Bergman, Elliot CS Shell Develop. Co., Emeryville, CA Journal of Organic Chemistry (1963), 28(9), 2210-15 SO CODEN: JOCEAH; ISSN: 0022-3263 DTJournal LAUnavailable GI For diagram(s), see printed CA Issue. Addition of di-chlorocarbene to norbornylene at 0° gave a C8H10Cl2 AB product isomeric with the expected dichlorocyclopropane derivative The isomer was shown to be 3,4-dichlorobicyclo[3.2.1]oct-2-ene (I). Similarly, cyclopentene gave a 40% yield of a 1:1 mixture of the normal product, 6,6-dichlorobicyclo[3.1.0]hexane (II) and its isomer, 2,3dichlorocyclohexene. The latter was shown to arise from the former during work-up. Addition of dichlorocarbene to cyclohexene and cycloheptene gave only normal (dichlorocyclopropane) products. The order of stability of the adducts described is consistent with strain being the controlling factor. A stable purple carbonium ion was formed by treatment of either dichlorocarbene adduct of cyclopentene with strong Lewis acids. Similarly were prepared other cyclo and bicyclo analogs. ANSWER 226 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN L5 AN 1963:419276 CAPLUS DN 59:19276 OREF 59:3449d-e Pure nuclear quadrupole resonances of several chlorinated cyclopropanes TT ΑU Todd, J. E.; Whitehead, M. A.; Weber, K. E. CS Univ. of Cincinnati, Cincinnati, OH SO Journal of Chemical Physics (1963), 39(2), 404-9 CODEN: JCPSA6; ISSN: 0021-9606 Journal DT LA Unavailable AΒ The nuclear quadrupole resonances of 5 chlorinated cyclopropanes are given, and the Cl frequencies are correlated with the effective orbital electronegativity of the C to which the Cl is bonded. The concept of mol. inequivalence of the Cl atoms is introduced in the interpretation of the temperature dependence of the frequencies in 2,2,2',2'tetrachlorobicyclopropane. L5 ANSWER 227 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN AN 1963:39664 CAPLUS DN 58:39664 OREF 58:6701h,6702h,6703a-b ΤI Cyclopropyl carbanion ΑU Walborsky, H. M. CS Fla. State Univ., Tallahassee SO Record Chem. Progr. (Kresge-Hooker Sci. Lib.) (1962), 23 (No. 2), 75-91 DTJournal LΑ

Unavailable
GI For diagram(s), see printed CA Issue.
AB Deuterium exchange of 2,2-diphenylcyclopropyl cyanide (I) in methanol-d had a half-life of 8 min., while the racemization of I had a half-life of 540 hrs. A barrier to inversion of I was inferred. 1-Bromo-1-methyl-2,2-diphenylcyclopropane (II), [α] -109°, with Na in refluxing PhMe gave 1-methyl-2,2-diphenylcyclopropane, [α] +89°, 30%

racemized, indicating major retention with some loss from the radical intermediate stage. II with Mg in tetrahydrofuran, yielded by carbonation 2,2-diphenyl-1-methylcyclopropanecarboxylic acid (III) with 12% optical purity. The same Grignard from II, BuLi, and Me2Mg.MgBr2, on treatment with 1,2-dimethoxyethane and CO2 gave III with complete retention of optical activity. The results were consistent with a radical mechanism of halide reaction with Mg. A review with 38 references was included.

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ANSWER 228 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
L5
AN
     1961:137111 CAPLUS
DN
     55:137111
OREF 55:25785e-h
     Cyclopropanes. IX. The relative and absolute configurations of
     1-substituted 2,2-diphenylcyclopropanecarboxylic acids
     Walborsky, H. M.; Barash, L.; Young, A. E.; Impastato, F. J.
AU
CS
     Florida State Univ., Tallahassee
so
     Journal of the American Chemical Society (1961), 83, 2517-25
     CODEN: JACSAT; ISSN: 0002-7863
DT
     Journal
LA
     Unavailable
os
     CASREACT 55:137111
AB
     cf. CA 55, 22231d. Each of the acids, 2,2-diphenylcyclopropanecarboxylic
     acid (I), 1-methyl-2,2-diphenylcyclopropanecarboxylic acid (II), and
     1-bromo-2,2-diphenylcyclopropanecarboxylic acid (III), formed a racemic
     compound Their order of stability according to thermal analysis and the
     Petterson scale was I » III > II. Thermal analyses revealed that
     (+)-II and (-)-III formed a quasi-racemic compound, that (+)-II and (+)-III
     yielded a solid solution, and no conclusive information on the mixts. of I
     and II, which was probably due to the unfavorable steric relationship of
     the two acids. Thermal analyses, x-ray powder diffraction patterns, and
     infrared analyses indicated that (-)-I and (+)-II, and (+)-II and (+)-III
     were configurationally related. Rotary dispersion curves of the resp.
     aldehydes of I, II, and III exhibited Cotton effects and further confirmed
     the related configurations. Tentative absolute configurations were assigned
     to (-)-I (S), (+)-II (S) and (+)-III (R) on the basis of the Prelog-Cram
     model and the known absolute configuration of (-)-menthol. A polymer
     configuration for the enantiomers and a dimer configuration for the
     racemates were suggested from an interpretation of the infrared spectra of
     these compds.
L5
    ANSWER 229 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN
AN
     1960:128371 CAPLUS
DN
     54:128371
OREF 54:24468h-i,24469a-b
     Relation between chemical structure and insecticidal activity in
     chlorocyclopropane derivatives
ΑU
     Komrsova, H.; Farkas, J.
CS
     Ceskoslov. akad. ved, Prague
SO
     Collection of Czechoslovak Chemical Communications (1960), 25,
     CODEN: CCCCAK; ISSN: 0010-0765
DT
     Journal
LΑ
     German
GI
     For diagram(s), see printed CA Issue.
     Adding portionwise, with intensive agitation and exclusion of moisture in
AΒ
     1 hr. at -40°, 5 g. freshly prepared KOCMe3 to 2.95 g.
     p-MeOC6H4CH:CMe2, 10 ml. CHCl3, and 100 ml. petr. ether (b.p.
     30-5°), stirring the mixture 3 hrs. (without cooling), washing with
     H2O to disappearance of the alkaline reaction, drying (Na2SO4), and evaporating
     gave 4 g. p-MeOC6H4-CH.CCl2.CMe2, m. 58-9° (n-hexane). Similarly,
     (p-ClC6H4)2C:CH2, PhCH:CH2, trans-PhCH:CHMe, cis-PhCH:CHMe, PhCH:CMe2,
     p-MeC6H4CH:CMe2, p-ClC6H4CH:CMe2, p-ClC6H4OCH:CH2 (I), cyclopentadiene
     (II) (m. 32°), and (Me2C:CH)2 gave with CCl2 (dichlorocarbene) the
     corresponding dichlorocyclopropane derivs. [b.p. and (or) m.p. (petr.
     ether) given]: m. 132-3°; b15 140°; b15 140°; b15
     140°; m. 33-4° and b8 118-20°; m. 62°; m.
     62-3°; m. 5° and b15 150°; b15 150°; m.
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78° and b15 150°. II added 1 equivalent CCl2 only. Addition of CCl2 failed with cis- and trans-stilbene, trans, trans-(PhCH:CH)2, and

PhCH:CHCO2Et. Cyclopropane derivs. prepared from I and II showed insecticidal activity on the house fly (L.D.50 0.3 and 0.9 γ , resp.). ANSWER 230 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN 1960:80425 CAPLUS 54:80425 OREF 54:15267a-d Cyclopropanes. VI. Retention of optical activity and configuration in the cyclopropyl carbanion Walborsky, H. M.; Impastato, F. J. Florida State Univ., Tallahassee Journal of the American Chemical Society (1959), 81, 5835-6 CODEN: JACSAT; ISSN: 0002-7863 Journal Unavailable cf. CA 53, 13100b. The determination of the effect of delocalization of the neg. charge on racemization of optically active compds. was attempted. CH2:CBrCO2Me with Ph2CN2 in the presence of alkali yielded 1-bromo-2,2-diphenylcyclopropanecarboxylic acid (I), m. 190-1°, which was resolved via the brucine salt to yield (+)-I, $[\alpha]$ 26D 111° (c 0.467) (all rotations in CHCl3). (+)-I with LiAlH4 yielded 1-bromo-2,2-diphenylcyclopropanecarbinol (II), m. 133-4°, [a] 109° (c 0.519). The tosylate of II (not isolated) with LiAlH4 yielded 1-bromo-1-methyl-2,2-diphenylcyclopropane (III), m. 84-5° [α] 106° (c 0.863). III (1.7 g.) in 50 ml. 1:1 C6H6-petr. ether cooled to 5°, treated during 20 min. with 0.05 mole BuLi in 50 ml. Et20 (temperature held below 6°), the mixture stirred 15 min. at 6°, and decomposed with MeOH yielded 0.342 g. 1-methyl2,2diphenylcyclopropane (IV), $[\alpha]$ 26D 78 \pm 1° (c 1.152). The rotation of -78° corresponded to an optical purity of 80.5% or to 60% retention and 40% racemization. (-)-2,2-Diphenylcyclopropanecarboxyli c acid (V) was configurationally related to (+)-1-methyl-2,2diphenylcyclopropanecarboxylic acid (VI) and (-)-V was related to (-)-IV. By the use of the Fredga quasi-racemate technique, (+)-VI was shown to have the same configuration as (+)-I. It therefore followed that the conversion of III to IV proceeded with over-all retention of configuration and there was retention of configuration in the cyclopropyl anion (60% at 6°). ANSWER 231 OF 231 CAPLUS COPYRIGHT 2006 ACS on STN 1957:12597 CAPLUS 51:12597 OREF 51:2616a-f Reactions of bivalent carbon compounds. Reactivities in olefin-dibromocarbene reactions Skell, Philip S.; Garner, Albert Y. Pennsylvania State Univ., University Park Journal of the American Chemical Society (1956), 78, 5430-3 CODEN: JACSAT; ISSN: 0002-7863 Journal Unavailable cf. C.A. 50, 14567e. Equimolar amts. of the appropriate olefin and CHBr3 in Me3COH treated at 0-3° with excess Me3COK at the rate of approx. 50 millimoles/hr., the mixture stirred 1 hr., and diluted with pentane and H2O, and the organic layer washed, dried, and evaporated gave the corresponding substituted 1,1-dibromocyclopropane derivs. (substituents, b.p./mm., nD25.0, % yield, and starting olefin given): 2-PhCH2, 104-6°/1, 1.5801, 13.3, PhCH2CH:CH2 (I); 2-Bu, 120-2°/58, 1.4905, 14.0, 1-hexene (II); 2,2-Me2, 65-6°/27, 1.5110, 65.1, Me2C:CH2 (III); 2,2-Ph2, -, - (m. 150-1°), 66.2, Ph2C:CH2 (IV); 2-(p-MeOC6H4), 3-Me(trans-), - (decomposition 155°), -, about 46.9, anethole (V); 2-Ph, 94°/2, 1.5963, 36.5, styrene (VI); 2,2,3,3-Me4, 93-4°/22, -(m. 77-8°), 54.0, (Me2C:)2 (VII); 2,2,3-Me3, 83°/24, 1.6134, 66.0, Me2C:CHMe (VIII); 2-CH2:CH, 70°/26, 1.5412, 72.0, (CH:CH2)2 (IX). Also prepared were (same data given): 7,7-Dibromobicyclo[4.1.0]heptane, 79-80°/2, 1.5560, 42.7, cyclohexene

(X); 6,6-dibromobicyclo[3.1.0]hexane, 110°/11, 1.5744, 54.2,

cyclopentene (XI). The relative rates of the 3-center addition of CBr2 to

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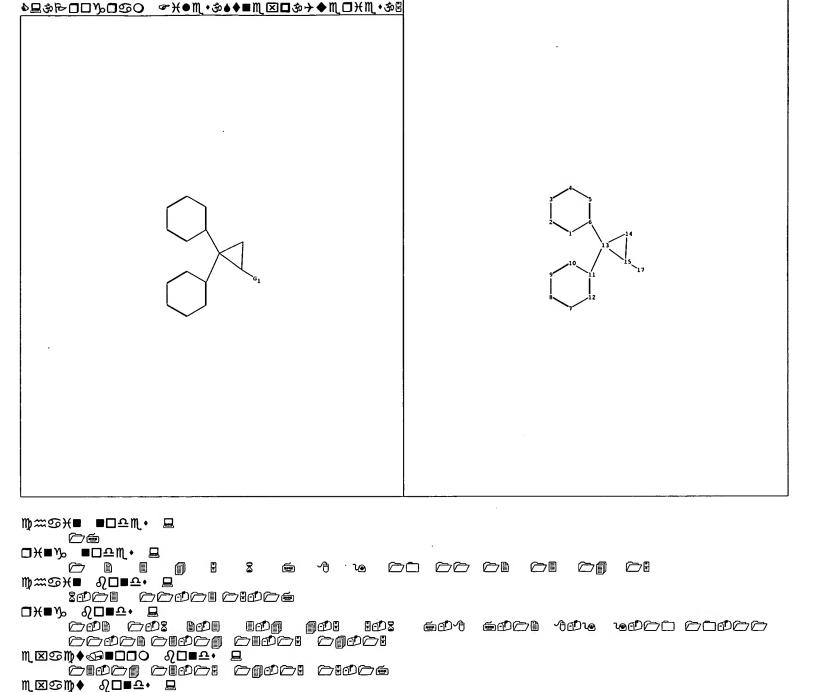
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LA AB the following olefins were: III 1.00, VII 3.5, VIII 3.2, V 1.2, IV 0.8, IX 0.5, XI 0.5, X 0.4, VI 0.4, II 0.07, I 0.02, CH2:CHBr very slow. The appropriate pairs of olefins treated slowly with cooling with CHBr3 in about 100 cc. Me3COH and with Me3COK in the usual manner [competing olefins and their initial M concns., M concns. of CHBr3 and Me3COK, g. yields of the olefins (in the order given), and ratio of rates of the reaction of the 2 olefins given]: III-II, 0:545-0.500, 0.199, 0.296, 28.2, 2.2, 13.9; VI-II, 0.500-0.500, 0.199, 0.431,30.1,6.4, 4.8; III-X, 0.541-0.500, 0.199, 0.296, 25.6, 10.4, 2.7; III-XI, 0.489-0.497, 0.199, 0.313, 23.0, 11.9, 2.2; VII-X, 0.200-0.800, 0.300, 0.221, 13.3, 6.5, 9.4; II-I, 0.131-0.131, 0.100, 0.116, 5.3, 2.1, 3.2; III-IV, 0.329-0.295, 0.200, 0.242, 21.6, 23.6, 1.3; VIII-X, 0.200-1.000, 0.200, 0.226, 15.8, 11.6, 8.6; V-III, 0.300-0.357, 0.200, 0.233, 23.9, 17.8, 1.2; IX-X, 0.670-0.643, 0.438, 0.538, 35.4, 29.4, 1.3.



*BABO